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**Novel Molecular Sources for Dispersing Boron in Carbon-Carbon  
Composites**

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Improving the oxidation resistance of carbon-carbon composites is key to expanding the use of this material system into higher temperature applications. While boron particles have been added to these materials to seal cracks in protective coatings, oxidation of the carbon matrix neighboring the boron particles seriously affects composite strength. This problem is exacerbated by a natural segregation of the boron particles to fiber rich areas of the composites. Carborane, a robust molecular source of boron, was used as the precursor for atomically dispersed boron in a phenolic derived carbon matrix. Modifications of the chemical structure of carborane were used to improve the solubility in phenolic. Additions of carboranes into the phenolic resins dramatically improved the oxidation resistance of the carbonized char. The char yield of the phenolic resin was also increased significantly.

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## Summary

Currently used boron-based carbon-carbon oxidation protection systems do not provide protection for the boron lean carbon matrix neighboring the boron particles. This problem is exacerbated by adding boron particles only during the initial prepregging and not during the impregnation cycles. The boron-lean matrix that results suffers severe oxidation when the protective coatings fail. By improving the oxidation resistance of the impregnated matrices through a chemically modified matrix forming resin, a long-life oxidation resistant carbon-carbon can be obtained. The Phase I program was designed to determine the feasibility of using carborane to atomically distribute boron through a carbon matrix.

Carboranes, a robust molecular source of boron, were chosen as the precursor for atomically dispersed boron. Phenolic resins were chosen as the precursor to the carbon matrix because of their relative simplicity, availability, cost and plethora of information concerning their pyrolysis.

The Phase I program was highly successful, additions of carborane into the phenolic resins dramatically improved the oxidation resistance of the carbonized char. It was also shown that the solubility of carborane in phenolic resin could be improved by modification of the chemical structure of carborane. The char yield of the phenolic resin was also increased significantly with the addition of a carborane. This improvement in char yield is expected to shorten the process time of carbon-carbon manufacturing.

The distribution of boron in the boron added chars, as studied by Scanning Auger Microscopy and X-ray Photoelectron Spectroscopy, indicated that carborane additions resulted in greater homogeneity than did particle additions. This homogeneity contributed to the achievement of greater oxidation resistance with less total boron addition. Good agreement was found between the results of boron characterization from Energy Dispersive Spectroscopy, Scanning Auger Microscopy and X-ray Photoelectron Spectroscopy.

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## Introduction

Carbon-carbon composites are attractive materials for use in applications requiring strength, low density and toughness at high temperatures. A serious drawback with these materials is that carbon reacts with oxygen; it oxidizes in air at temperatures above 425°C. To improve the oxidation resistance of carbon-carbon composites, molecular sources for atomically dispersing boron in the carbon matrix were explored. The use of boron as a sealant, through the formation of a boron oxide glass on the surface of the carbon-carbon, has been used, but the distribution of boron in these carbon-carbon materials has not been uniform. Added as particulate to prepreg cloths, but not into the resin or liquid pitch precursors used for impregnation (due to the viscosity limitation), results in boron segregation to fiber rich areas. This leaves large amounts of the carbon matrix susceptible to oxidation. Atomically dispersed boron, provided in the impregnate, was proposed as a means to improve the oxidation resistance of the inhibited carbon-carbons.

To prove feasibility, the Phase I program had the following primary objectives:

- To identify and synthesize suitable boron-carbon precursors for the fabrication of the carbon matrix
- To characterize the pyrolysis behavior of selected boron/carbon precursor systems
- To characterize the distribution and compositional state of boron in the carbon matrix
- To determine the oxidation behavior of the carbonized precursor system
- To assess the potential of atomically dispersed boron as an oxidation inhibitor for carbon-carbons based on the results of the proposed study.

The Phase I work plan was divided into the five following tasks:

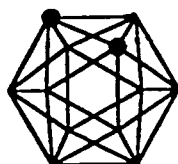
- Task 1. Identification, Synthesis and Characterization of Boron Precursors
- Task 2. Fabrication of Boron/Carbon Oxidation Samples
- Task 3. Analysis of Boron Distribution and Oxidation State
- Task 4. Characterization of Oxidation Resistance
- Task 5. Final Report

## Results and Discussion

### Task 1. Identification, Synthesis and Characterization of Boron Precursors

Carborane (1), a robust molecular source of boron ( $C_2B_{10}H_{12}$ ), was chosen as an additive to provide the boron molecule required for the oxidation resistance of phenolics. Phenolic resin chemistry had been well studied and many references are available in the open literature.<sup>1</sup> Phenolic resin consists of a phenolic group

interspersed with a methylene group. They are formed by a condensation reaction between phenol and formaldehyde, with elimination of water.



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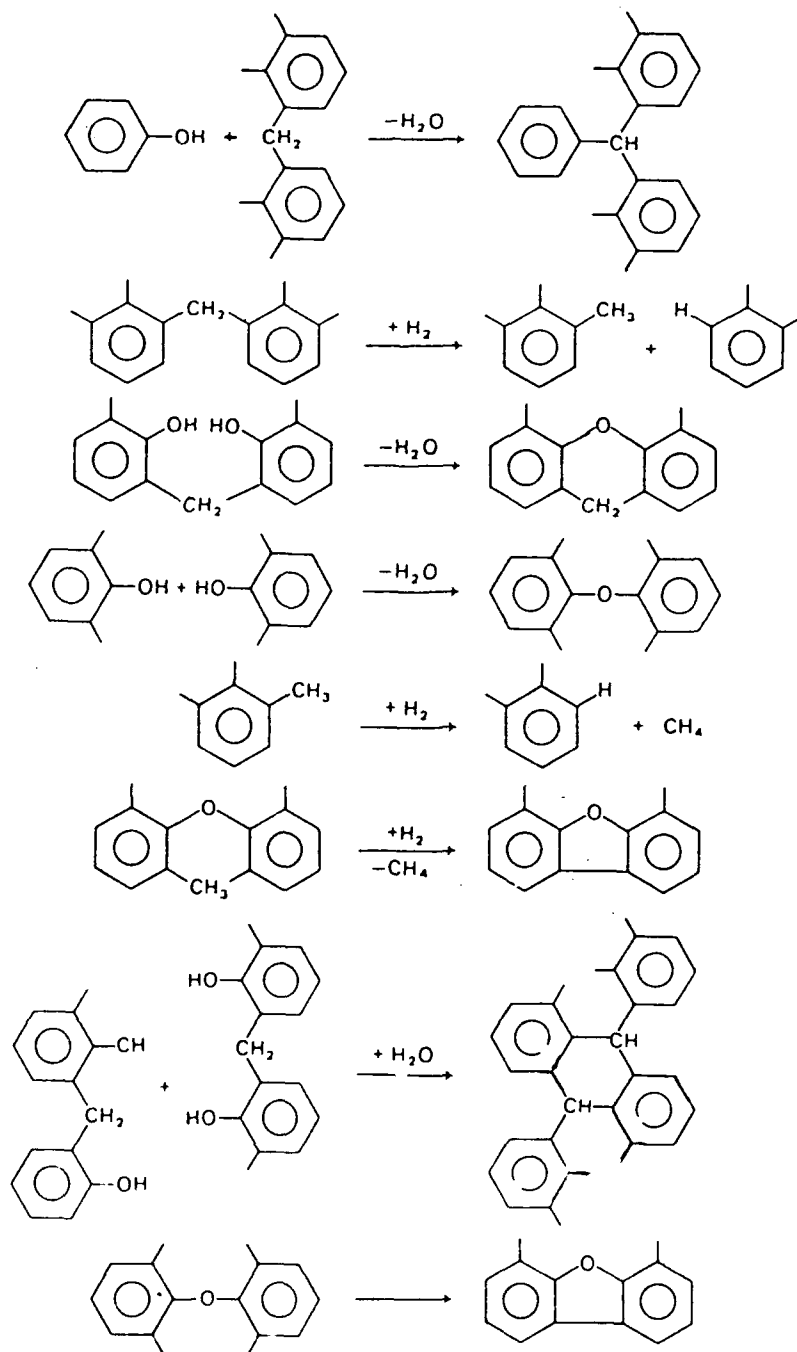
Phenol is reacted with excess formaldehyde and heated in the presence of alkaline catalysts such as sodium hydroxide or ammonia. The reaction is interrupted at an early stage, so that the actual degree of polycondensation is carried out to either the A- or B- stage resins. The A-stage resin, called 'Resol', is a relatively short, low molecular weight, linear polymer. The B-stage resin, called 'resitol', is a long linear polymer with a slight amount of cross-linking between chains. A- and B-resins are used for laminates. Heating to a higher temperature causes extensive cross-linking and the formation of a hard and rigid solid, the infusible and insoluble C-stage resin.

Figure 1 shows the possible reactions that occur during the pyrolysis of phenolic resins. Hydroxyl groups on neighboring chains condense to form ether linkages as the temperature approaches 300°C. Simultaneously, the hydroxyl group may react with the methylene group in a neighboring chain to form a closer cross-link similar to the diphenylmethane structure. During condensation, water is formed from the free hydroxyl groups during these reactions. Subsequently, the methylene bridge ruptures, forming methane as a by-product.

Borden SL359A resin was originally identified as a commonly used resin for this study. The high viscosity of this phenolic, 10,000 to 20,000 CPS, made mixing with the carboranes difficult. Consequently, a less viscous resin, Borden SC1008 with a viscosity of 180-500 CPS, was used in this work. SC1008, a resin with 30% isopropyl alcohol (IPA) solvent, has a chemical composition similar to that of SL359A and is also commonly used in the fabrication of carbon-carbon composites. High purity, o-carborane, commercially available from Dexsil Corp., Hamden, CT, was used as baseline additive.

Substitution of ligands on the carborane cage was proposed as a means of improving the solubility of carborane in phenolics. Syntheses of the modified carboranes were carried out at Princeton University by Dr. Kaixu Yuan and Professor Maitland Jones. The compound of 2-Naphthyl 1-o-carboranylmethyl ether (NCME) was synthesized according to the literature.<sup>2</sup> A benzene (400ml) solution of decaborane (12.89 g, 0.11 mole), 2-naphthyl 3-butynyl-1 ether (19.20 g, 0.11 mole), acetonitrile (28.82 g, 0.70 mole) was heated to the reflux point for 12 hours. Decaborane was purchased from Callery Chemical Company. 2-Naphthyl 3-butynyl-1 ether was prepared by the literature method.<sup>3</sup> After the reaction, the solvent was removed under reduced pressure. The remaining yellow oil was recrystallized in an ethanol and water solution. Drying of the compound gave a white crystal (22 g, 71% yield). A second recrystallization yielded the final product.





**Figure 1. Possible Reactions during the Pyrolysis of Phenolic Resins**

To accommodate the non-dispersive properties of the phenolic resin, a slight modification of the side group of the carborane compound was proposed. The compound can be rendered less dispersive by adding a carboxylic acid into the side

group. Synthesis of the modified carborane, 4'-carboxylic acid phenyl 1-o-carboranymethyl ether (CAPCME) was performed in two steps. The intermediate for the CAPCME, 4'-methyl benzoate carbonyl ether, was synthesized according to the literature.<sup>2</sup> A benzene (300ml) solution of decaborane (19.13 g., 0.16 mole, 1.0 equiv.), 4'-methyl benzoate 3-butynyl-1 ether (29.97 g., 0.16 mole), acetonitrile (21.51 g., 0.52 mole) was heated to the reflux point for 22 hours. The solution was washed with 2X200 ml 10% HCl, 200 ml H<sub>2</sub>O, 2X200 ml saturated NaCl solution and dried with anhydrous MgSO<sub>4</sub>. The reaction product was then filtered and the solvent was removed under a reduced pressure. The resulting yellow oil could not be recrystallized in ethanol and hexane solution. Drying of this compound gave a jelly-like paste. (46.25 g., 95% yield)

Hydrolysis of this intermediate gave the final product. 4'-methyl benzoate carbonyl ether (46 g., 0.15 mole) was dissolved in 400 ml ethanol and drop-wise added into 14.12 grams of NaOH in 100 ml H<sub>2</sub>O. The solution was stirred for 17 hours and then acidified with concentrated HCl and extracted with 2X300 ml of ether. The organic layer was washed with 2X300 ml of 10% HCl, 500 ml H<sub>2</sub>O and 500 ml saturated NaCl solution. The organic layer was then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtration and evaporation of the resulting solution gave a white solid (27.10 g., 62% yield). Recrystallization in ethanol and water yielded the CAPCME.

Synthesis of the modified carborane, 1-methyl-2-carboxylic acid-o-carborane (MCAC), was again performed according to the literature.<sup>4</sup> A n-BuLi hexane solution (110 ml, 2.35 M, 0.26 mole, 1.3 equiv.) with 300 ml tetrahydrofuran (THF) solvent was drop-wise added into methyl-o-carborane (31.63 g., 0.20 mole, 1.0 equiv.) in 200 ml THF. Methyl-o-carborane was purchased from Czechoslovakia. The reaction vessel was immersed in an ice-water bath. The solution was then stirred at room temperature for 10 hours. The resulting solution was poured on 1000 grams of dry ice in a large beaker and stirred vigorously. After evaporation of the solvent at room temperature for 18 hours, the resulting slurry was added to 700 ml of benzene. The aqueous solution was acidified with concentrated HCl and extracted with 600 and 2X200 ml of ether. The ether layer was washed with 1000 ml of H<sub>2</sub>O, 500 ml of concentrated NaCl and dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent yielded a yellow solid. The final product, MCAC, was obtained by recrystallization in benzene and hexane.

The synthesized compounds were characterized with Fourier Transform Infrared Spectroscopy (FTIR), nuclear magnetic resonance (NMR), gas chromatography (GC), thin layer chromatography (TLC), high resolution mass spectrometry (HR-MS), melting point determination and elemental chemical analysis. Melting point was measured with a Thomas-Hoover capillary melting point apparatus and was not corrected. TLC was taken on a 0.25 mm silica gel layer with fluorescent indicator UV-254.

Analytical GC was performed on a Hewlett-Packard 5890 chromatograph equipped with a Hewlett-Packard 3390A integrator, using a 0.75 mm I.D., 60m SPB-1 glass column. FTIR was recorded on a Nicolet 5DBX spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a GE-300 NMR spectrometer. DIP-

MS and HR-MS spectra were carried out on KRATOS 50 RFA high-resolution mass spectrometer. Elemental analysis was performed at Galbraith Laboratory (Knoxville, Tenn.) using carbon/hydrogen elemental analyzer and induction coupled plasma (ICP). Table I shows the results of the characterization tests. Elemental chemical analyses suggests the potential of these molecules for oxidation protection. The relatively low numbers of percent C and H from elemental analysis of NCME was probably due to incomplete oxidation.  $B_2O_3$ , from the oxidation of boron, probably prevented the complete burn-up of the specimen. The discrepancy between the theoretical and analytical boron content can be attributed to experimental error. Due to this experimental error, no elemental analysis was performed on the CAPCME and MCAC compounds.

### Task 2. Fabrication of Boron/Carbon Oxidation Samples

The focus of this task was to fabricate glassy carbon disks for subsequent characterization and evaluation. This task also provided information regarding the solubility and yields of the carboranes selected from Task 1.

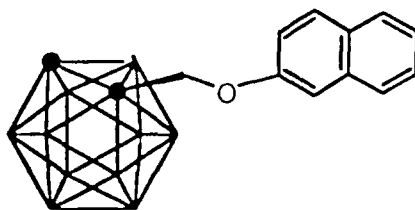
Five (5) and twenty (20) wt.% of o-carborane was added to the phenolic resin. After stirring at room temperature for one hour, excess IPA, a solvent, was removed by vacuum evacuation. Prior to the evaporation of the excess solvent, the 20% o-carborane sample appeared cloudy. Curing of this sample at 40°C resulted in the separation of undissolved compound. This undissolved material floated to the surface and foamed during the subsequent curing process. A thin layer of void free carborane saturated phenolic was obtained. Similarly, 5% of the 2-naphthyl 1-o-carboranylmethyl ether (NCME) additions the SC1008 resin resulted in a cloudy solution. A 60°C heat treatment increased the solubility of the NCME in SC1008. Only a trace amount of undissolved NCME was detected visually on the top of the resin. Due to this apparent limitation of solubility, the 20% NCME sample was not prepared. The CAPCME compound performed similar to that of NCME, i.e., the solubility in SC1008 resin was slightly less than 5%. On the other hand, the MCAC sample showed significantly greater solubility in SC1008. Additions of 8.3 and 24.5% of MCAC samples were prepared. With a 53.5% boron content in this compound, the boron content in carbonized chars would be around 8.23 and 21.4 %, barring any evaporation of boron during the carbonization process. Conventional boron powder containing phenolics were also prepared using micron size  $ZrB_2$  and sub-micron boron powders.

The solubility of non-electrolytes is determined by the net effect of the entropy of mixing and heat of mixing. The entropy of mixing is dominated mainly by the system temperature and the melting point of the solute while the heat of mixing is controlled by the solubility parameters of the solute and solvent. The solubility parameter is defined as the square root of the cohesive energy density. If the solubility of solute and solvent are equal the system behaves like an ideal solution. Solubility parameter can be broken down into contributions from three interaction types: dispersion, dipole and hydrogen-bonding. To achieve high solubility the dispersive, polar, and hydrogen bonding components of solubility parameters of the solute and solvent should be similar. Since IPA is a good solvent for phenolics and is characterized as strongly hydrogen bonding, phenolics can be described

similarly. Hydrogen bonding may explain the reduction in solubility of carborane in resin when a naphthoxide, a strong dispersive compound, was added into the carborane. Additions of functional groups also reduce the boron content of the carborane molecules; therefore, only significant improvements in solubility warrant modification of the carborane molecule.

**Table I(a). Analysis of Naphthyl 1-o-carboranylmethyl ether**

Molecular structure:



Molecular formula: **C<sub>13</sub>H<sub>20</sub>B<sub>10</sub>O**.

Formular weight: 300.25.

Melting point: 97°C.

TLC (hexane): R<sub>f</sub> = 0.20.

GC (ethanol solvent): RT = 27.53 min.

FT-IR (Mineral oil): 2860, 2586, 1218 cm<sup>-1</sup>.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.2-3.2 (b., 10H), 4.16 (s, 1H), 4.54 (s, 2H), 7.06-7.80 (b., 7H) ppm.

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub>): 58.84, 69.63, 72.30, 108.03, 118.52, 125.16, 127.46 (2C), 128.27, 130.18, 130.54, 134.68, 155.53 ppm.

DIP-MS: 300 (M<sup>+</sup>, 75%), 143 (40%), 127 (20%), 115 (100%), 77 (5%).

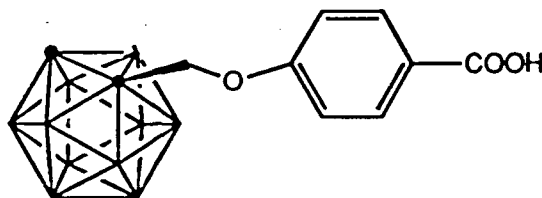
HR-MS: M<sup>+</sup>, calc: 300.2518; found: 300.2524.

**Elemental Chemical Analysis:**

	% Carbon	% Hydrogen	% Boron
	32.15	6.05	30.49
	32.05	5.99	30.68
theoretical value	52.00	6.67	36.00

**Table 1(b). Analysis of 4'-carboxylic acid phenyl  
1-o-carboranymethyl ether**

Molecular structure:



Molecular formula: **C<sub>10</sub>H<sub>18</sub>B<sub>10</sub>O<sub>3</sub>**.

Formular weight: 294.24.

Melting point: 256-259°C.

TLC (50% ethyl actate/50%hexane): R<sub>f</sub> = 0.53.

GC (decomposes on the GC).

FT-IR (Mineral oil): 3150, 2587, 1674, 1606, 1296, 1245 cm<sup>-1</sup>.

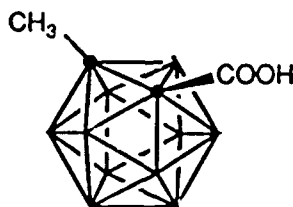
<sup>1</sup>H NMR (300 MHz, d<sup>6</sup>-acetone): 1.2-3.5 (b., 10H), 4.72 (s, 2H), 4.91 (s, 1H), 7.05 (d, 2H), 7.98 (d, 2H), 10.5 (b. s. 1H) ppm.

<sup>13</sup>C NMR (75 MHz, d<sup>6</sup>-acetone): 61.17, 69.59, 73.31, 115.11, 124.72 (2C), 132.28, 132.36, 161.61, 167.14 ppm.

DIP-MS: 294 (M<sup>+</sup>, 100%), 277 (20%), 249 (20%), 253 (28%), 121 (12%).

**Table 1(c). Analysis of 1-methyl-2-carboxylic acid-o-carborane**

Molecular structure:



Molecular formula: **C<sub>4</sub>H<sub>14</sub>B<sub>10</sub>O<sub>2</sub>**.

Formular weight: 202.21.

Melting point: 197-199°C.

TLC (33% ethyl acetate/77%hexane):  $R_f = 0.60$ .

GC (decomposes to methyl-*o*-carborane on the GC)

FT-IR (Mineral oil): 2860, 2587, 1725, 1250  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.2-3.2 (b., 10H), 2.17 (s. 3H), 8.0 (b. s., 1H) ppm.

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 24.41, 74.62, 76.80, 160.32 ppm.

MS: no  $\text{M}^+$  peak, 187 (25%), 156 (33%), 128 (40%), 101 (18%), 78 (100%).

The prepared resins were poured into aluminum dishes and cured in air under various cycles. The manufacturer recommended curing cycle was used successfully to cure a neat SC1008 resin. To accommodate the addition of carborane, this cycle was slightly modified by slowing the heating rate in the temperature range of 80-100°C. MCAC/SC1008 samples foamed at 70°C and required an even slower heating rate. This low temperature foaming might be attributed to the carboxylic acid side group to the carborane cage as they decomposed on GC analysis. A further reduction of heating cycle was required for the curing of boron powder added system due to the addition of a significant amount of surface moisture from sub-micron powders. Table 2 lists the curing cycles for the neat, carborane and boron powder added SC1008 resins.

**Table II(a) Curing Cycle for SC1008 Phenolic Resin**

<u>Time (hours)</u>	<u>Temperature (°C)</u>
24	40
72	60
24	71
24	85
24	99
24	113
72	127
24	138

**Table II(b) Curing Cycle for Carborane added SC1008**

<u>Time (hours)</u>	<u>Temperature (°C)</u>
24	40
24	60
24	70
72	80
24	90
24	100
24	113
24	127

**Table II(c) Curing Cycle for Boron Powder Added SC1008**

<u>Time (hours)</u>	<u>Temperature (°C)</u>
24	60
24	70
24	75
72	80
24	85
24	90
24	95
24	100
72	105
24	115
24	127

The cured phenolic resins were cut into small pieces and carbonized under a nitrogen atmosphere under the following conditions:

20°C	to	300°C	0.5°C/min. heating rate
300°C	to	600°C	0.3°C/min. heating rate
600°C	to	900°C	0.5°C/min. heating rate

Long processing cycles has been one of the main reasons for the high cost of the carbon-carbon materials. The relatively low yield of the phenolic and the extremely slow heat treatment cycle required to prevent foaming during the carbonization are responsible for this long process time. Table III lists the char yields of the phenolic resin and additions of carboranes. Additions of carborane significantly increased the char yield of phenolics. Increases in char yield should reduce the numbers of impregnation/densification steps required to achieve high density in the carbon-carbon composites. Also it is known that additions of borate and phosphate reduce the foaming of carbonaceous materials.<sup>5</sup> Consequently,

additions of carborane into phenolic resin may also prevent foaming and afford a much faster carbonization cycle.

**Table III. Char Yields of the Phenolic Resins**

<u>Material</u>	<u>Char Yield (%)</u>
SC1008	58.49±0.42
4.7% CAPCME	67.04±0.51
5% NCME	67.34±0.56
5% Carborane	74.78±0.55
8.3% MCAC	71.17±0.76
"20%" Carborane	77.62±0.63

The base-line and modified phenolic chars were oxidized in air at 900°C for one hour to determine oxidation behavior. (At temperatures above 900°C the coating cracks in oxidation protected carbon-carbons are mechanically closed and chemically sealed by oxide formation.<sup>6</sup>) Table IV lists the weight losses of this oxidation test. The unmodified phenolic char was completely consumed during this test while the weight losses of the boron added chars were dramatically reduced. The additions of as little as 5% carborane into phenolic resin improved the oxidation resistance over 10 times.

**Table IV. Weight Losses of the Phenolic Resins**

<u>Materials</u>	<u>% Weight Loss</u>
SC1008	100.00
5% NCME	16.64
4.7% CAPCME	10.61
5% Carborane	10.87
8.3% MCAC	7.35
"20%" Carborane	5.34



SEM/EDS was used to characterize morphology and determine the boron content of the phenolic chars prior to and after the oxidation test. Figures 2 to 8 show the results. Elemental boron cannot be detected in the EDS analysis; consequently, the oxygen peak from  $H_3BO_3$ , a product of boron hydrolysis, was used as an indicator of boron content in these chars. It was also assumed that there was no boron loss during the carbonization process.

Carbon was the only element detected in the as-carbonized carborane/SC1008 char. As the sample hydrolyzed, as detected by weight gain, the oxygen peak in the energy dispersive spectra increased. Figures 9 and 10 show the weight gain and O:C ratio of the 4.7% CAPCME/SC1008 char as function of time in contact with air. Both percent weight gain and O:C ratio depend linearly on the exposure time in the first 48 hours. No oxygen peak was detected in the fresh char indicating that the EDS has a low sensitivity to  $B_2O_3$  analysis. The O:C ratio remained constant while the percent weight gain increased slowly after the first 48 hours. The weight gain in the first 48 hours corresponds to the hydrolyzation of  $B_2O_3$ , while the subsequent weight gain is presumed due to adsorption of surface moisture.

Surface adsorbed moisture was not detected by EDS analysis. The SC1008 char picked-up about 4% surface moisture after 50 days in air. Part of this surface adsorbed moisture (0.8%) was removed by evacuation in the SEM and no oxygen peak was detected on this 3.2% weight gained sample. A linear relationship exists between weight gain and O/C ratio during the hydrolyzation of  $B_2O_3$  (Figure 11). The O/C ratio of the 4.7% CAPCME after 48 hours is about the same as that of 5% NCME sample which has a similar boron content and exposure time. To make use of the EDS oxygen peak as an indicator for boron content, samples must be hydrolyzed under the same condition.

Most of the chars showed a smooth surface with cracks produced from shrinkage. Only carbon was detected on the SC1008 char. The 5% carborane added sample showed a ratio of oxygen to carbon peak height (O:C) of 0.36 and 0.33 after 48 hours of air exposure on the top and bottom surface, respectively, indicating a uniform distribution of boron in the char. A few tiny pin holes were observed on the bottom surface of the char. The 5% NCME sample showed an O:C of 0.21 and 0.17 on the top and bottom surface, respectively. The reduction of the oxygen (and boron) peak in the NCME added sample was believed to be due to lower boron content in NCME. There is 75 and 36% boron in carborane and NCME molecules respectively. The slightly higher O/C on the top surface can be attributed to the undissolved NCME. The 20% carborane addition showed an O/C of 0.63 and 0.60 on the top and bottom surface, respectively. Figures 12 and 13 show the SEM/EDS results of the oxidized 5% carborane added sample. Only oxygen was detected in this sample.

Based on the boron content of the carboranes and the char yield of the as-cured phenolic resins, the boron contents of the 5% o-carborane and 5% NCME sample were calculated to be about 4.78 and 2.55%, respectively. No corrections were made based on the amount of IPA solvent evaporated and yield of the curing process. (about 30% weight loss) This is used to compensate the sublimation of



Figure 2(a). SEM of SC1008 Char

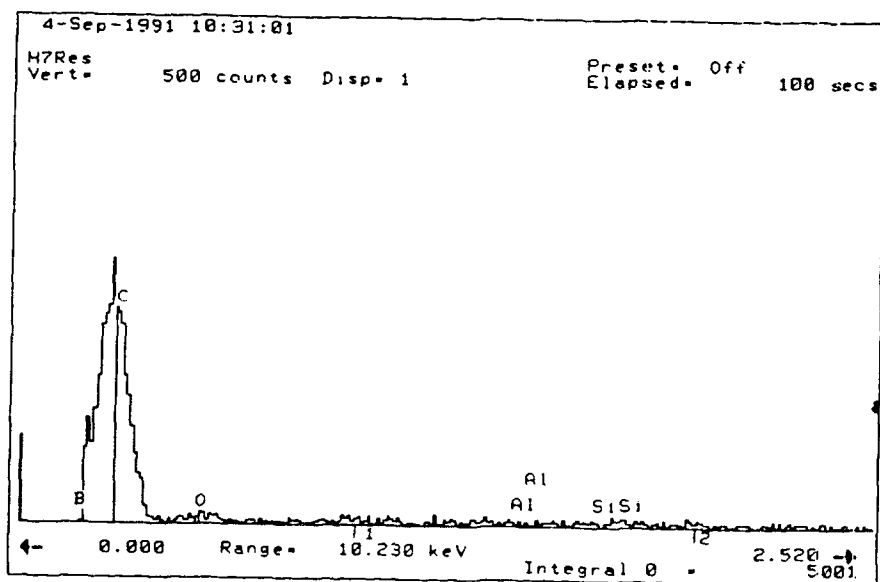
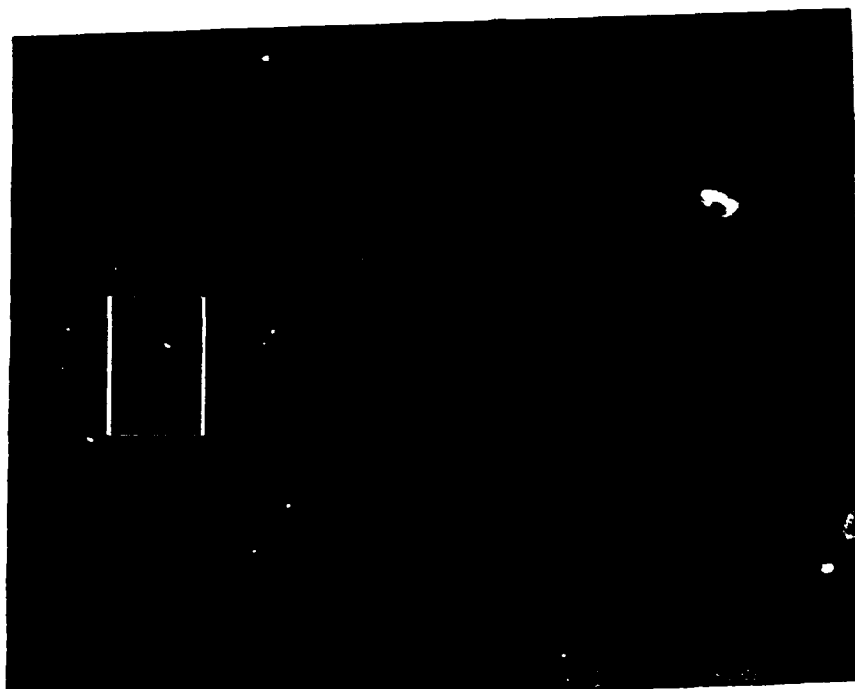
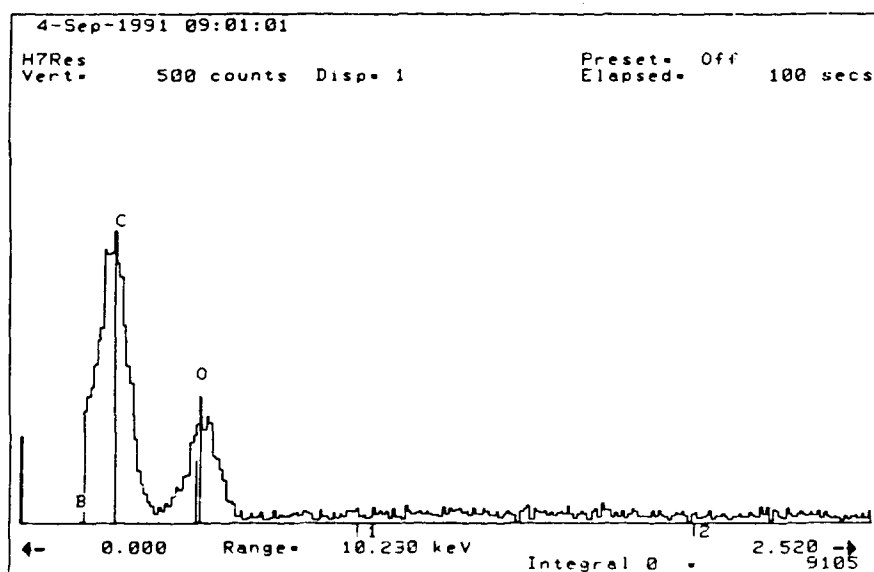


Figure 2(b). EDS of SC1008 Char



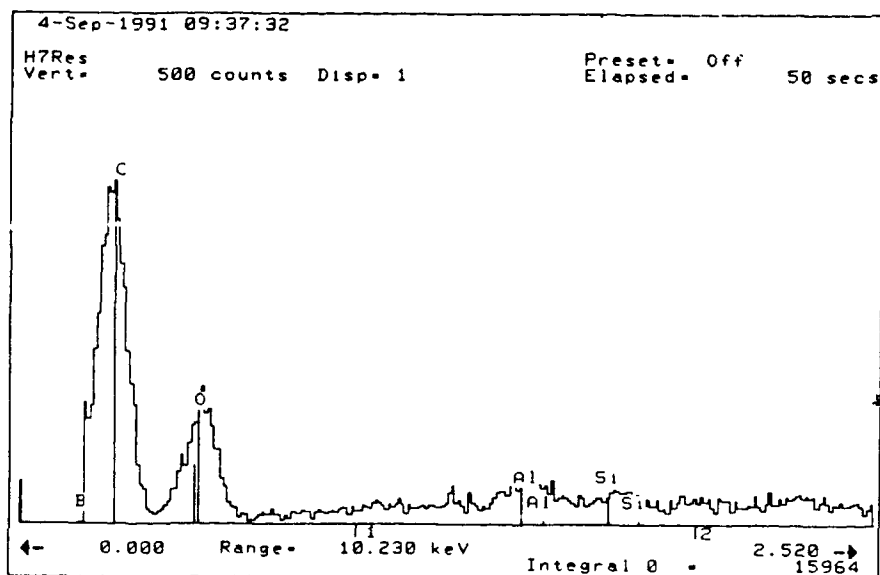
**Figure 3(a). SEM of 5% o-Carborane Added SC1008 Char (Top)**



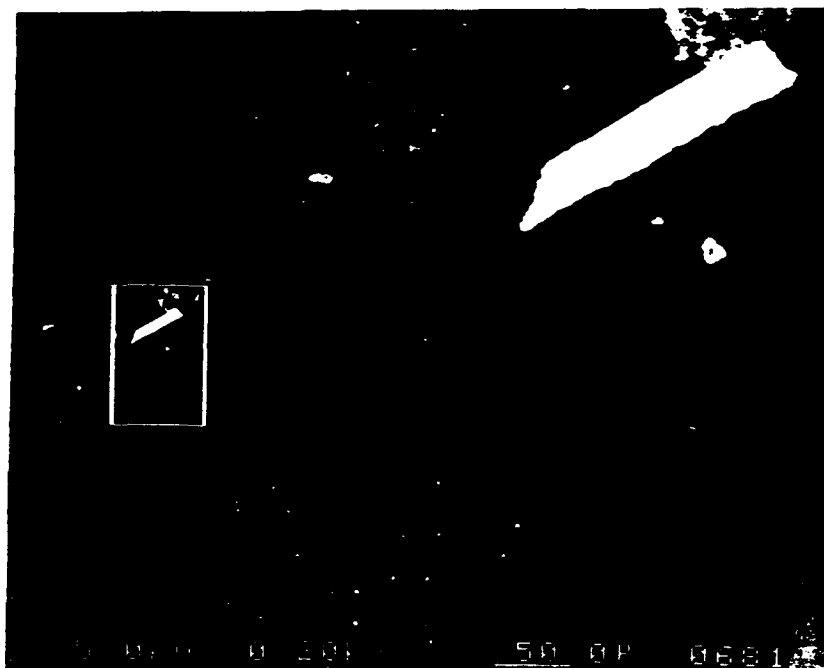
**Figure 3(b). EDS of 5% o-Carborane Added SC1008 Char (Top)**



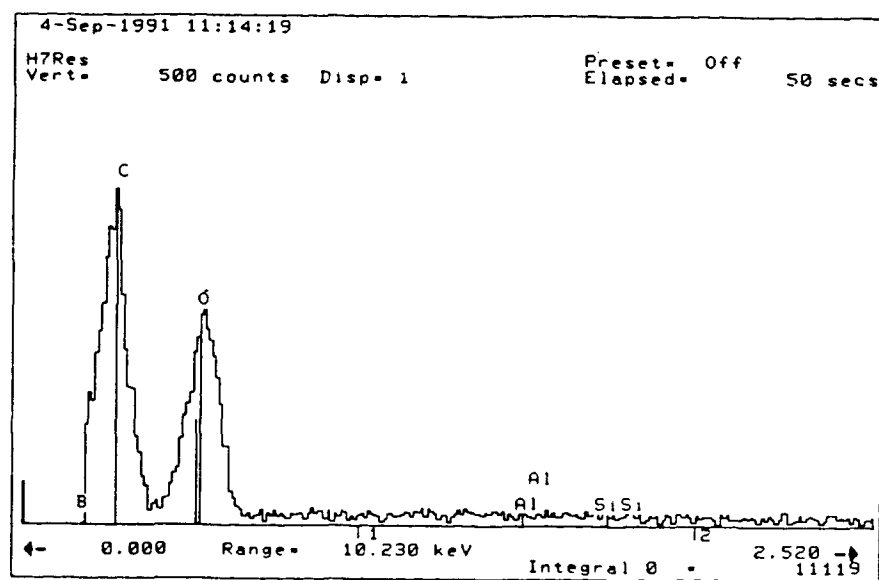
**Figure 4(a). SEM of 5% o-Carborane Added SC1008 Char (Bottom)**



**Figure 4(b). EDS of 5% o-Carborane Added SC1008 Char (Bottom)**



**Figure 5(a). SEM of "20%" o-Carborane Added SC1008 Char (Top)**



**Figure 5(b). EDS of "20%" o-Carborane Added SC1008 Char (Top)**

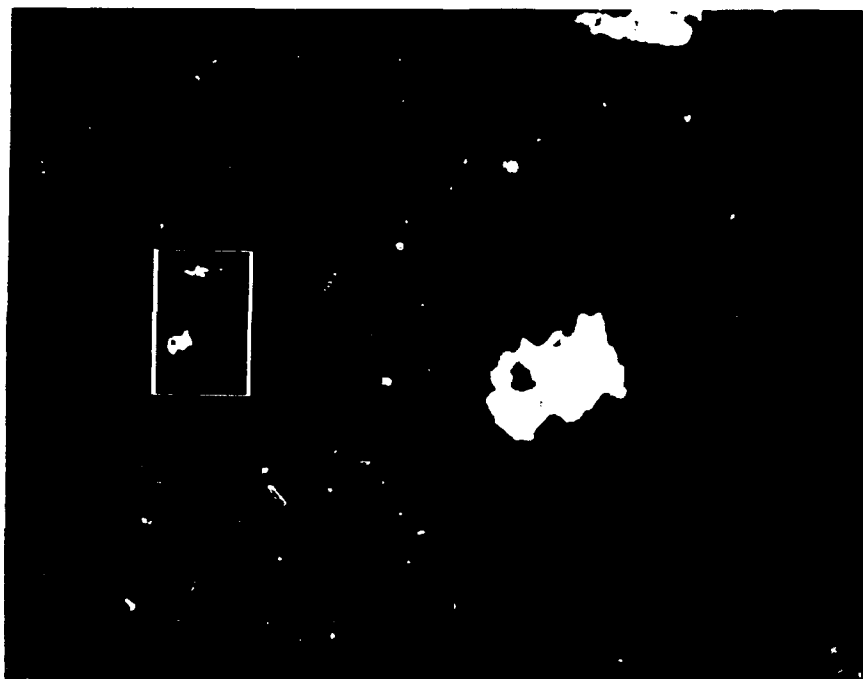


Figure 6(a). EDS of "20%" o-Carborane Added SC1008 Char (Bottom)

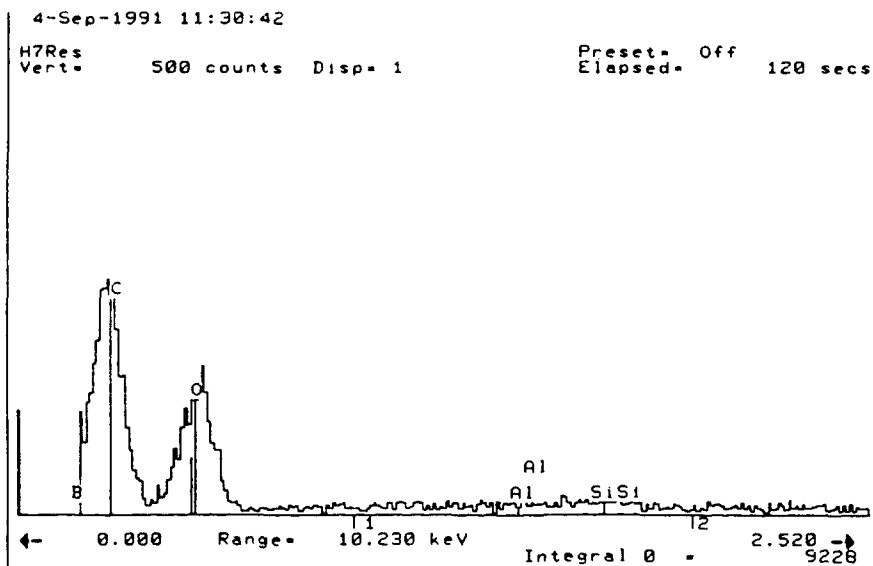
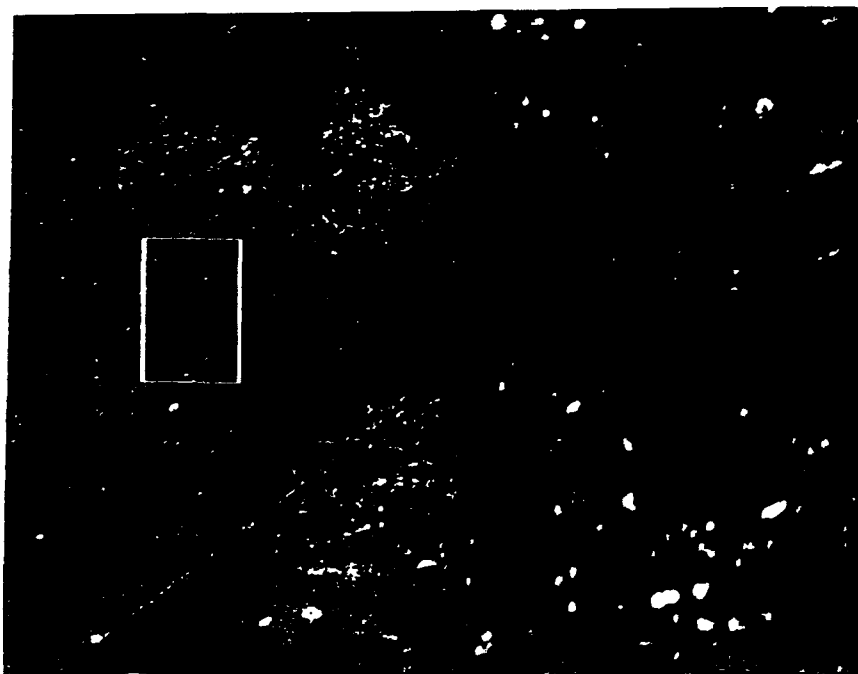
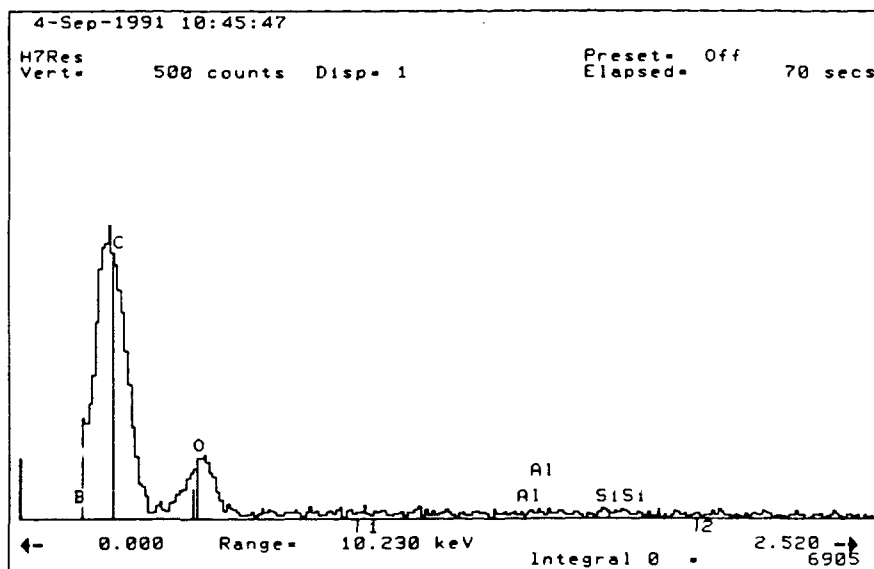


Figure 6(b). EDS of "20%" o-Carborane Added SC1008 Char (Bottom)



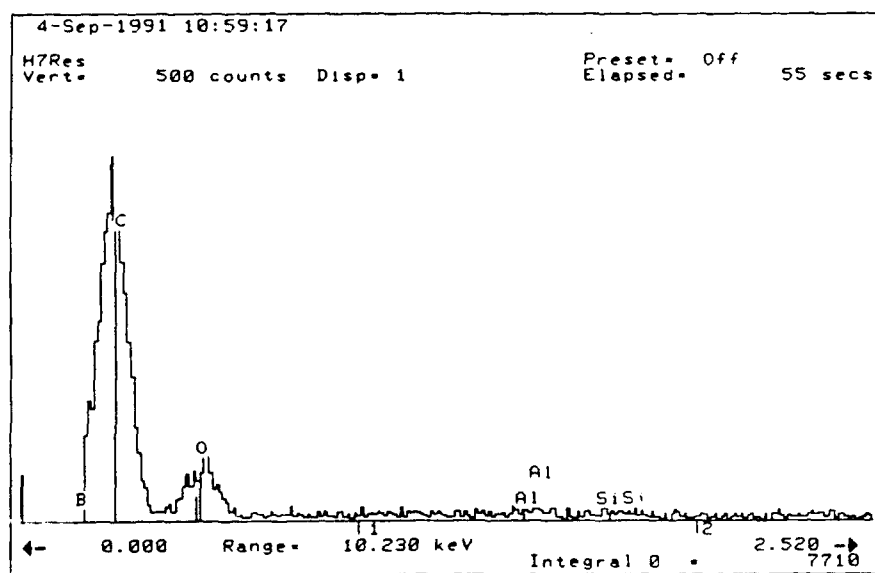
**Figure 7(a). SEM of 5% NCME Added SC1008 Char (Top)**



**Figure 7(b). EDS of 5% NCME Added SC1008 Char (Top)**

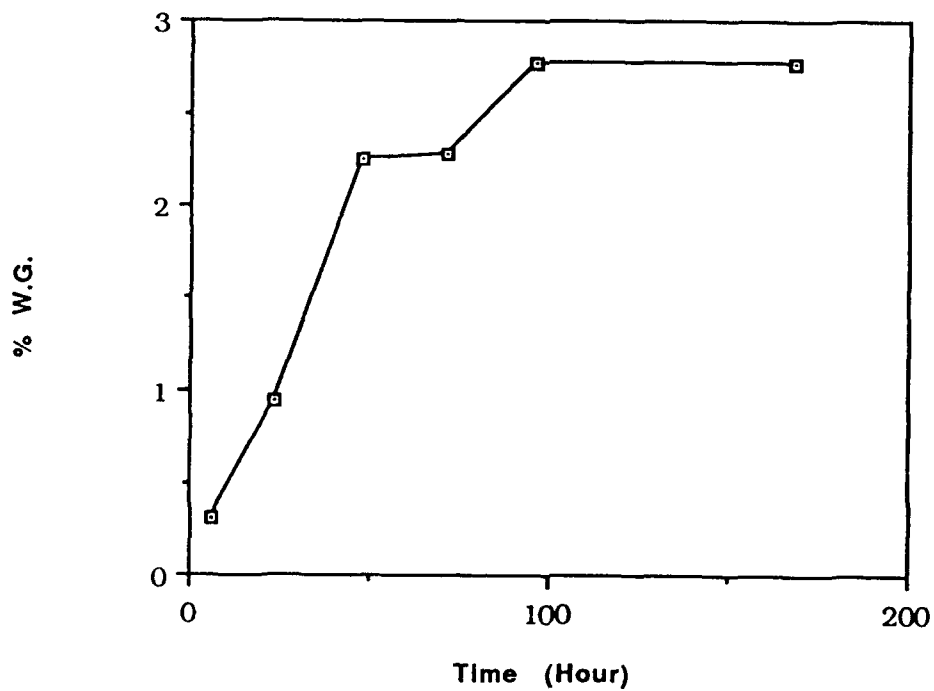


**Figure 8(a). SEM of 5% NCME Added SC1008 Char (Bottom)**

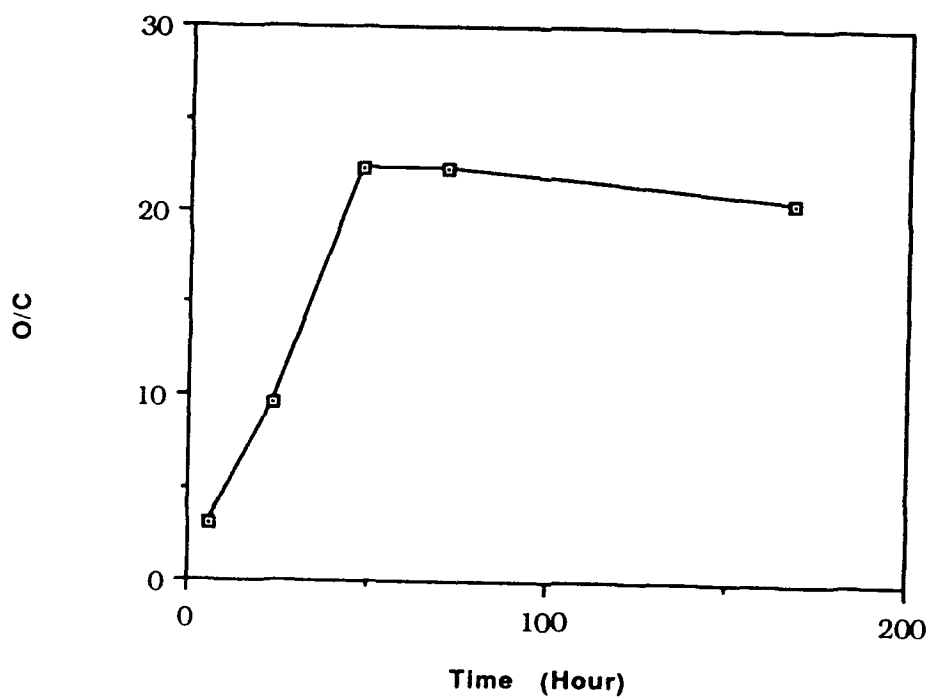


**Figure 8(b). EDS of 5% NCME Added SC1008 Char (Bottom)**

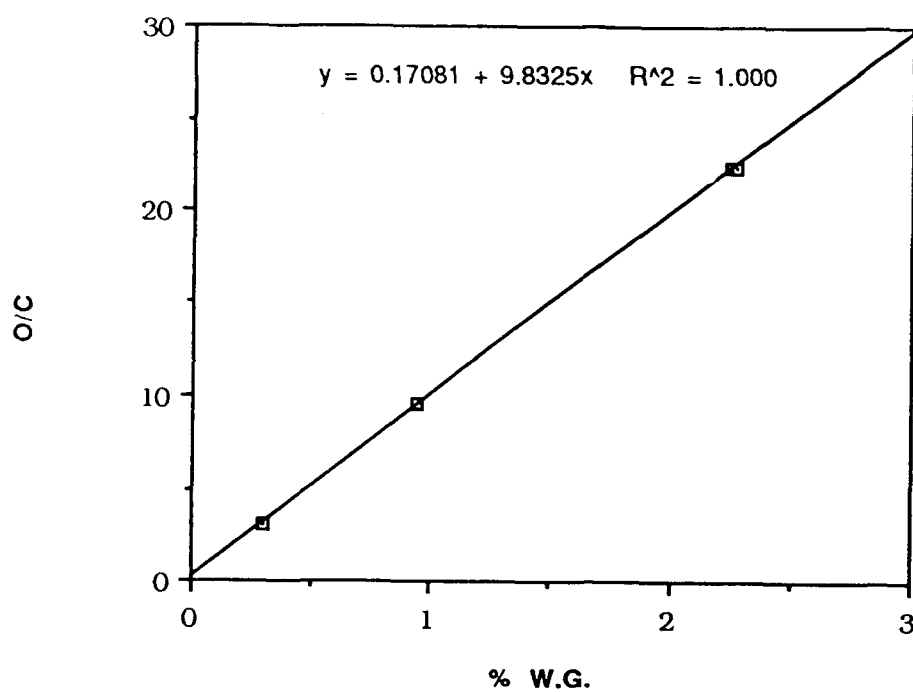




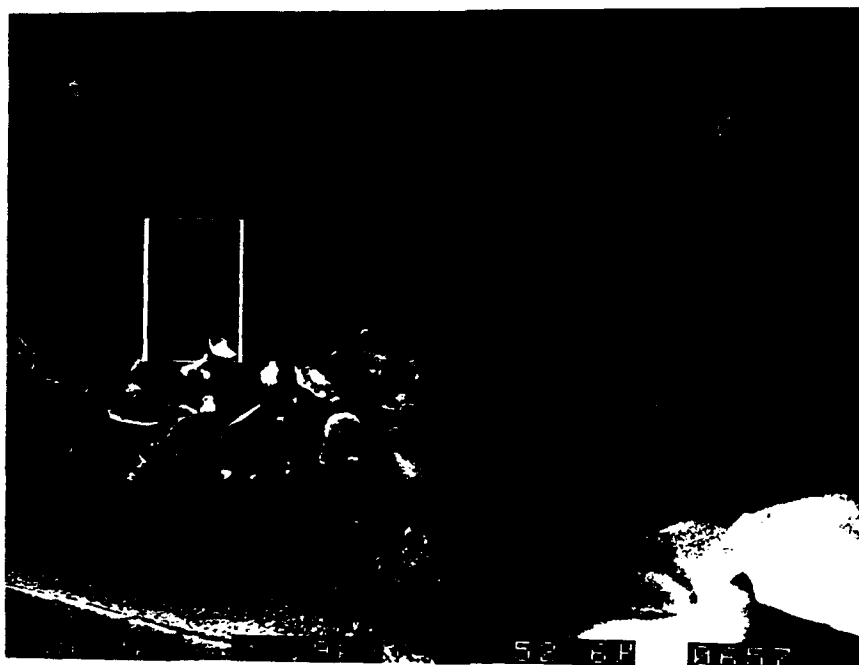
**Figure 9. Weight v.s.Exposure Time of 4.7% CAPCME Char**



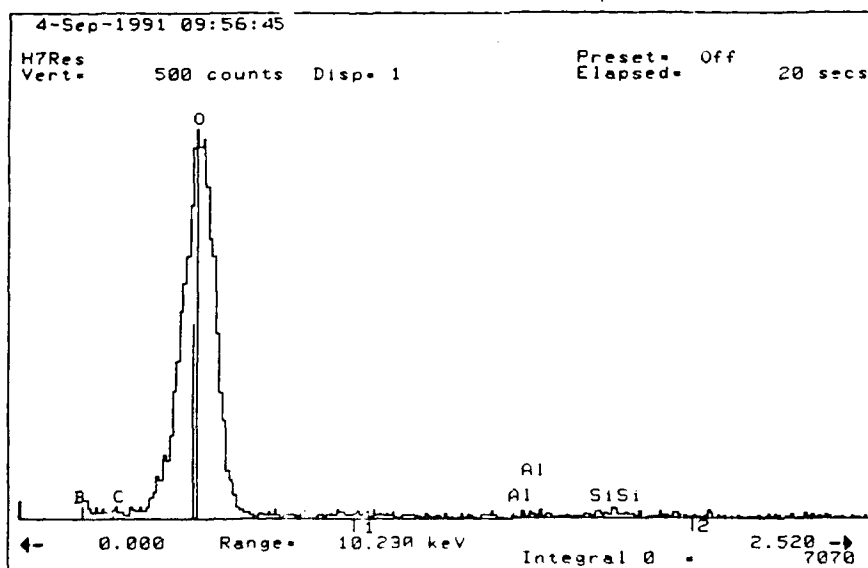
**Figure 10. O/C Ratio v.s. Exposure Time of 4.7% CAPCME Char**



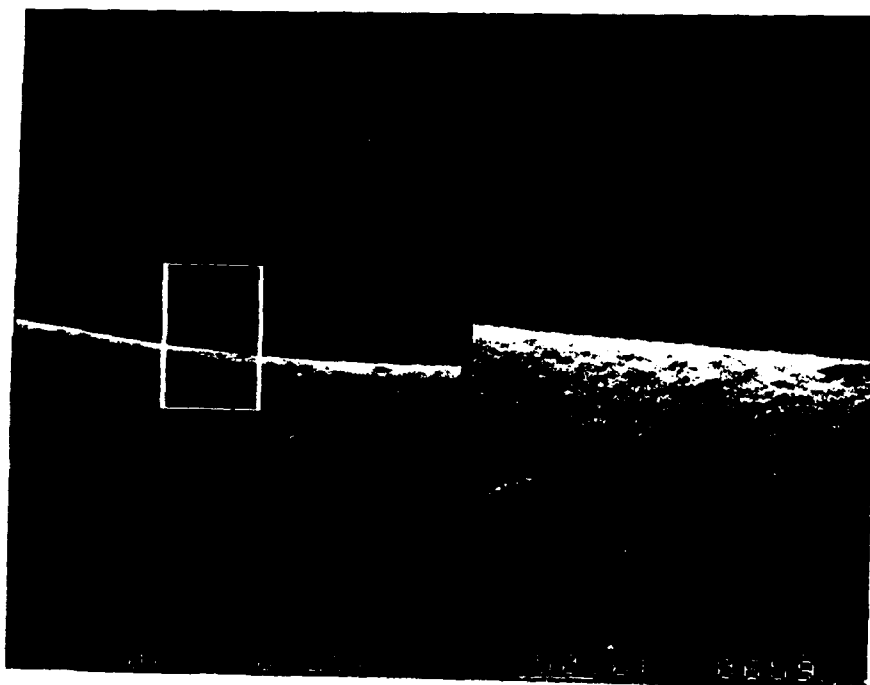
**Figure 11. Weight Gain v.s. O/C Ratio of 4.7% NCME Added Char**



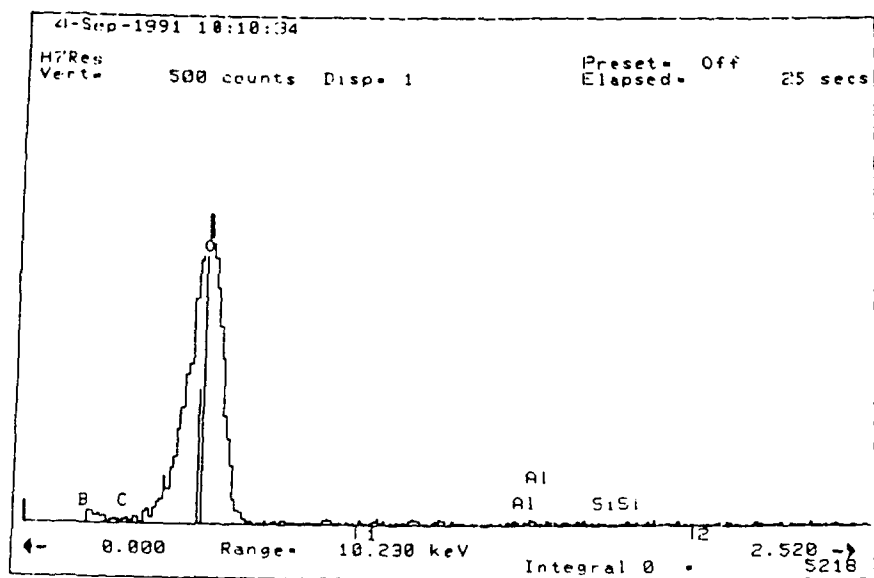
**Figure 12(a). SEM of the Oxidized 5% o-Carborane Added Char (Top)**



**Figure 12(b). EDS of the Oxidized 5% o-Carborane Added Char (Top)**



**Figure 13(a). SEM of the Oxidized 5% o-Carborane Added Char (Bottom)**



**Figure 13(b). EDS of the Oxidized 5% o-Carborane Added Char (Bottom)**

carborane. (see Task 3) From the measured O:C ratios of these chars, the boron content of the 20% carborane and 5% NCME chars were calculated to be 8.52 and 2.63%, respectively. The agreement of the boron content of 5% NCME char calculated from O:C ratio and boron content /char yield indicated that the assumption of no boron evaporation during the carbonization process was probably correct. (The other possibility was that all of the samples lost about the same percentage of boron during the carbonization process.) Given the 8.52% boron content in the 20% carborane char, the solubility of the carborane in SC1008 phenolic resin was estimated to be about 9.67%.

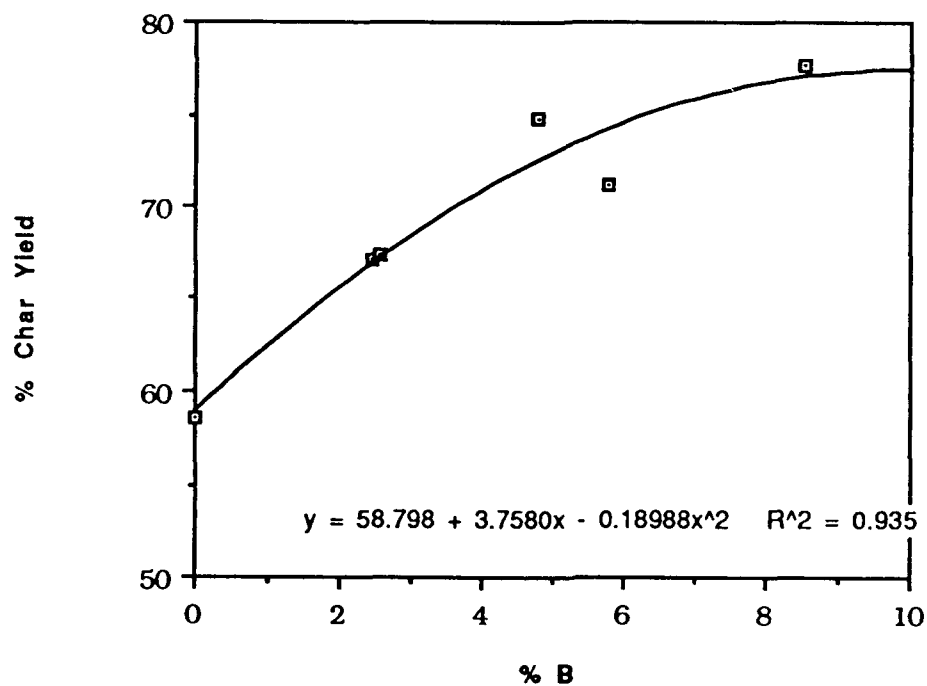
Figure 14 shows the relationships between the boron content and char yield of the phenolic chars. The large surface area of the MCAC added SC1008 (due to foaming) may be responsible for the low char yield. The boron added samples showed a significant improvement in the char yield. This extra yield was attributed to the reactions between added boron and phenolic molecules. Figure 15 shows the relationships between the boron content and weight loss at 900°C of the chars. Small amounts of boron addition dramatically improved the oxidation resistance of phenolic char. Extrapolation of the weight loss vs. boron content curve indicates that a boron content of 11.3% (or about 13.4% carborane) is required for complete oxidation protection. This is significantly less than the ~40% boron required for the powder added samples.

Figures 16 to 19 show the SEM/EDS results of the boron powder additions before and after oxidation. The boron powder char shows clusters of  $B_2O_3$  on the top and flaky surface on the bottom. This flaky surface was identified by X-ray diffraction to be zirconium diboride ( $ZrB_2$ ). (Figure 20) No boron powder was detected. However, the huge O:C ratio observed in this sample was attributed to the high concentration of boron powder. Sedimentation of high density  $ZrB_2$  powder is probably responsible for the smaller carbon peak noted on the bottom surface. Yet little zirconium was detected in this sample. Oxidation at 900°C for one hour produced  $B_2O_3$  on the surface of the boron powder/SC1008. Mud cracks with a thickness of about 4  $\mu m$  were observed on the bottom surface. X-ray diffraction and EDS results identified this cracked layer to be amorphous  $B_2O_3$ .

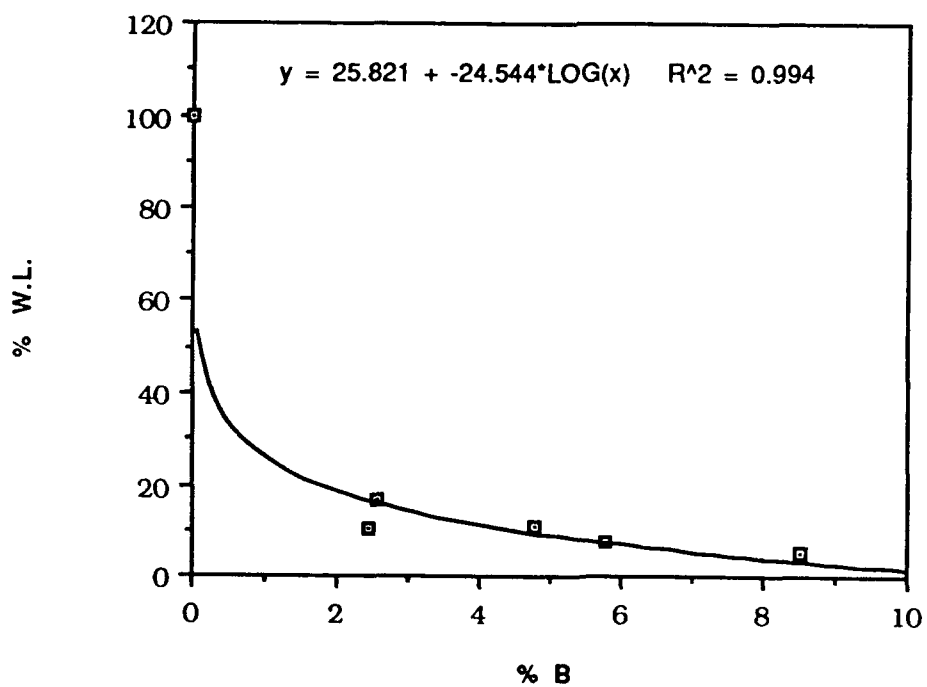
### Task 3. Analysis of Boron Distribution and Oxidation State

The distribution of boron and the oxidation states present in the glassy carbon were determined using Auger electron spectroscopy and X-ray photoelectron spectroscopy. This work was performed at Harvard University by Dr. Per Uvdal and Professor Cynthia Friend. Scanning Auger electron spectroscopy (SAM) was used to measure the dispersion of the boron on the surface of the carbon-carbon materials. The boron distribution in the bulk material was also measured by analyzing the cleaved surface. The boron Auger electron energy (179 eV) is well separated from that of carbon (272 eV) so that analysis for boron is straightforward.

The carbon samples were degassed in a vacuum desiccator (100°C) overnight prior to the Auger analysis. Without this treatment the outgassing of adsorbed moisture



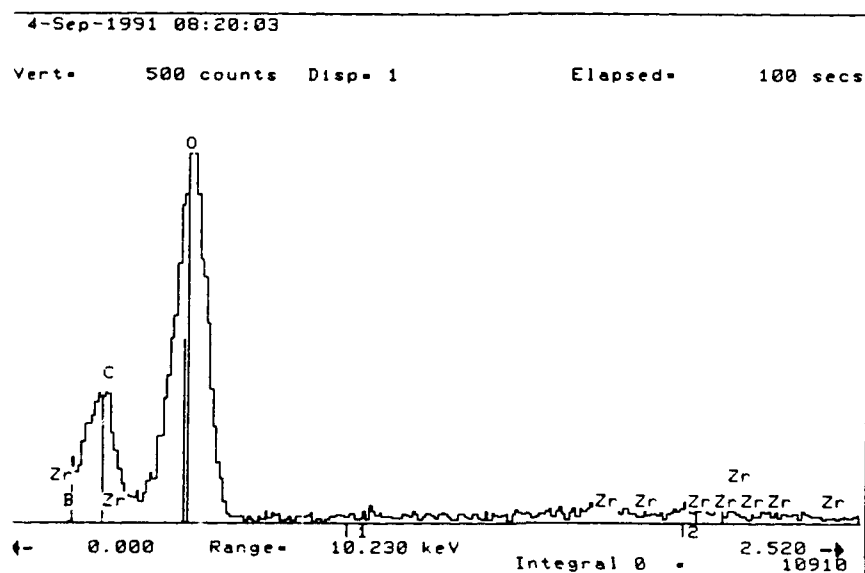
**Figure 14. Char Yields of Boron Added SC1008 Phenolics**



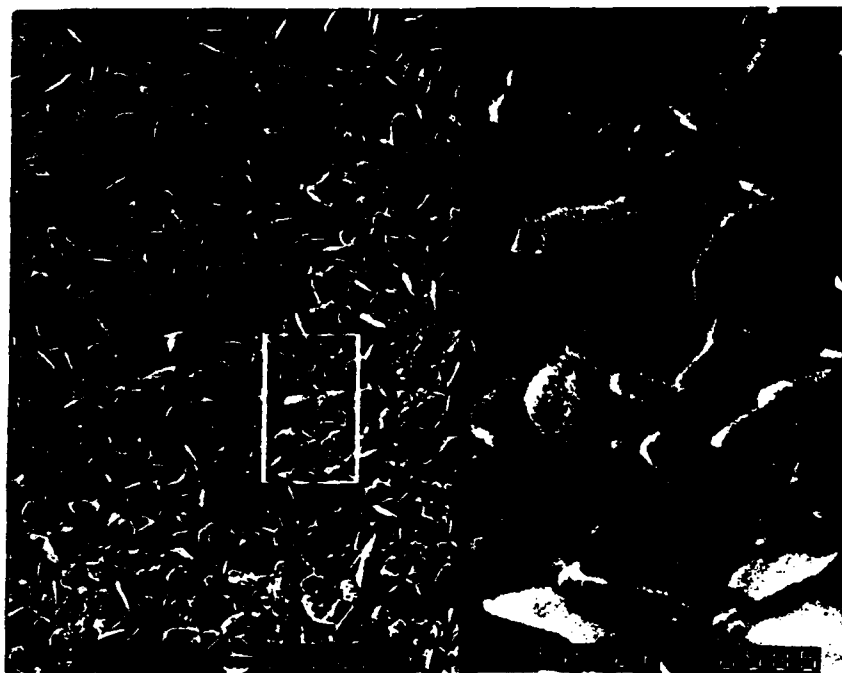
**Figure 15. Weight Loss of Boron Added SC1008 Chars**



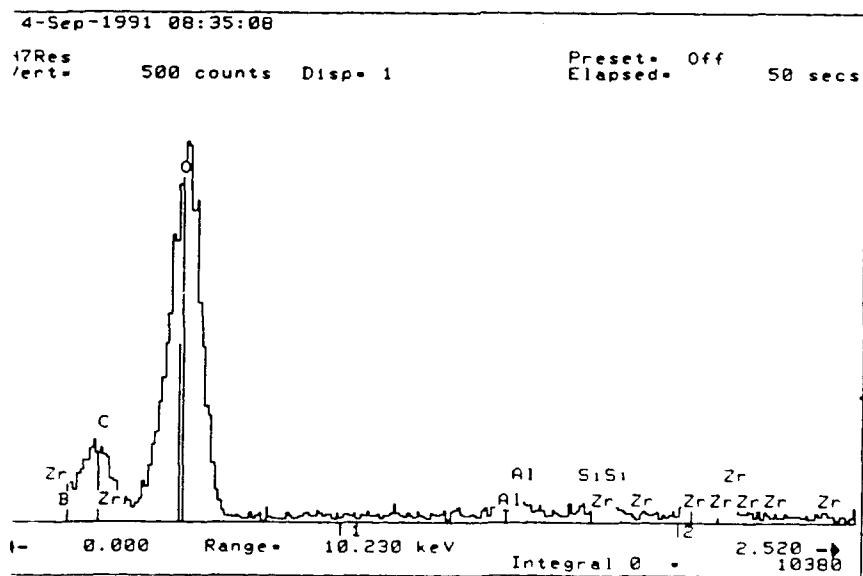
**Figure 16(a). SEM of Boron Powder Added SC1008 Char (Top)**



**Figure 16(b). EDS of Boron Powder added SC1008 Char (Top)**

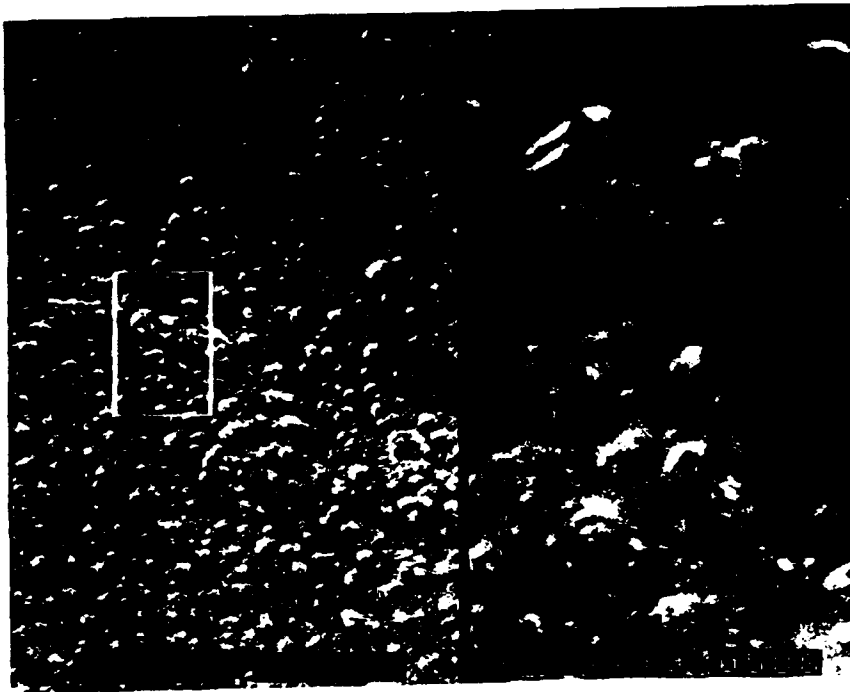


**Figure 17(a). SEM of Boron Powder Added SC1008 Char (Bottom)**

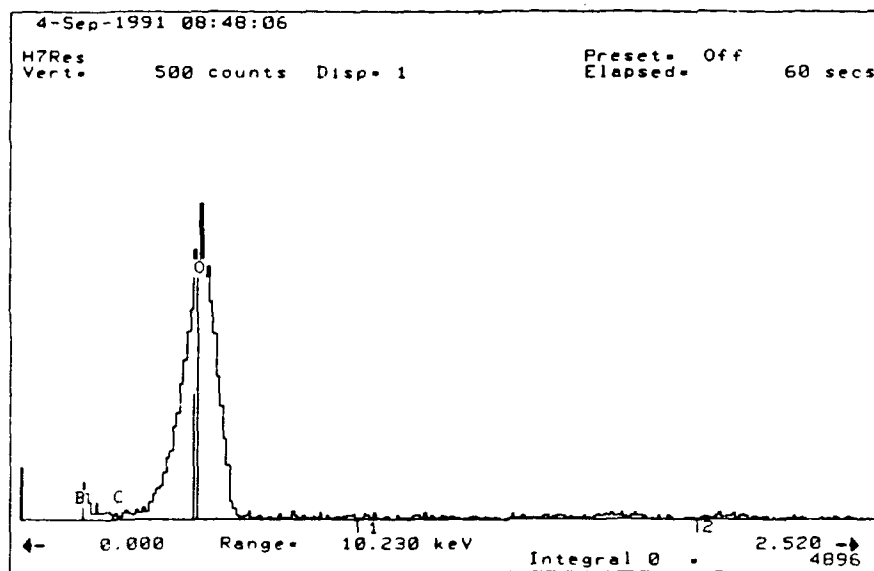


**Figure 17(b). EDS of Boron Powder Added SC1008 Char (Bottom)**





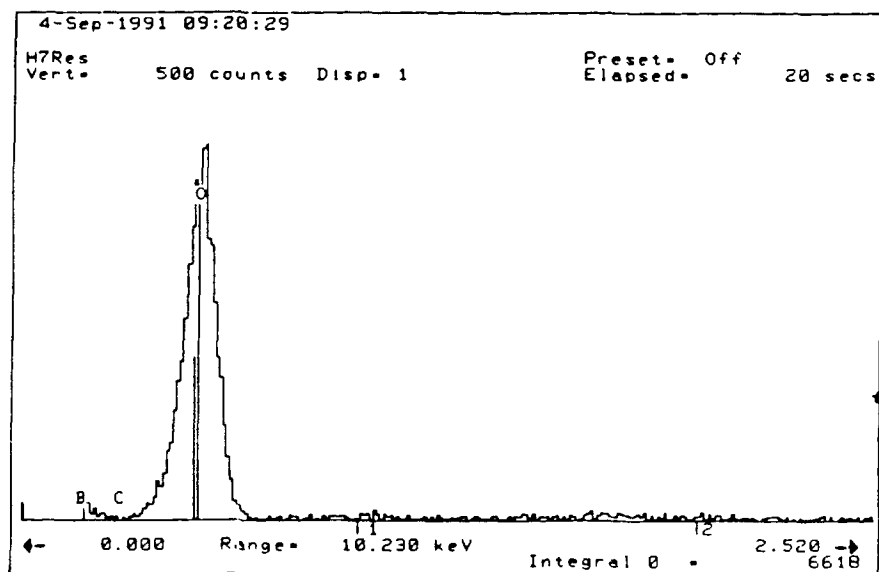
**Figure 18(a). SEM of the Oxidized Boron Powder Added Char (Top)**



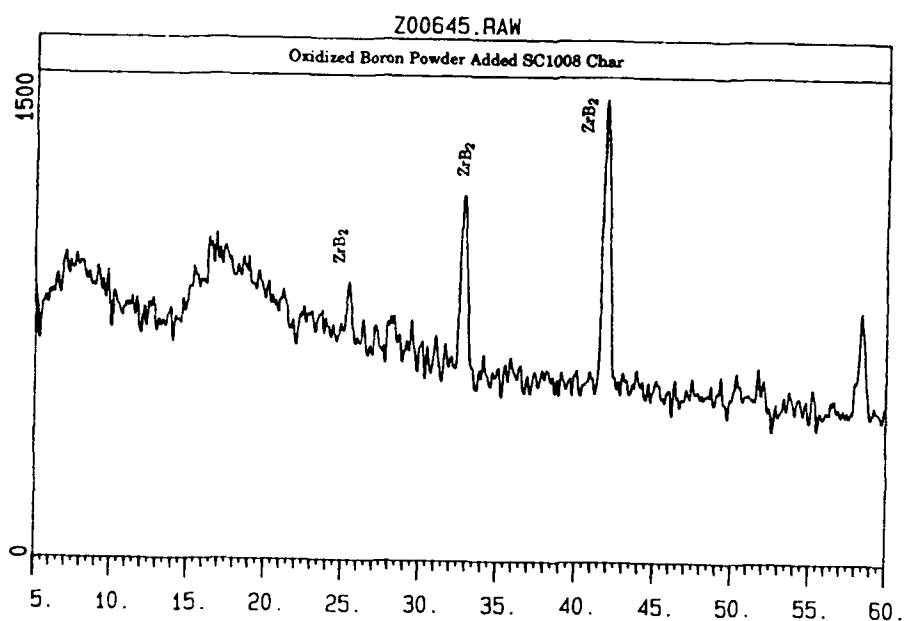
**Figure 18(b). EDS of the Oxidized Boron Powder Added Char (Top)**



**Figure 19(a). SEM of the Oxidized Boron Powder Added Char (Bottom)**



**Figure 19(b). EDS of the Oxidized Boron Powder Added Char (Bottom)**



**Figure 20. X-Ray Diffraction Pattern of the Flaky Surface of Oxidized Boron Powder Added SC1008 Char**

was too great to achieve satisfactory vacuum. A four minute sputtering was used to further clean the surface of 5% carborane added SC1008 char. Table V listed the B:C and B:O ratios of this sample. The boron signal of this sample was very weak which makes these B:C and B:O ratios less reliable.

**Table V. Scanning Auger Microscopy Results of 5% o-Carborane Added SC1008 Char**

	Surface	Bulk
B:C	0.056	0.043
B:O	0.16	0.39

The 20% o-carborane added SC1008 char produced more boron signal than the 5% sample. The 20% sample is likely to show the greatest amount of segregation. An increase of the boron signal was also observed for a sputtering time of to six minutes. The homogeneity of the sample was investigated by probing B:C ratios in three different areas, table VI shows the B:C ratios. A fluctuation of less than 20% of the average was observed in the B:C ratios.

**Table VI B:C ratios of 20% o-Carborane Added SC1008 Char**

	Area 1	Area 2	Area 3
B:C	0.073	0.103	0.082
Deviation from Average (%)	-15.1	19.8	-4.6

Table VII shows the B:C and B:O ratios of the boron powder added sample. Varying the degree of sputtering resulted in a significant difference of the B:O ratios. SEM examination of this sample (Figure 16) also revealed a inhomogeneous morphology. SAM analysis of a particle exhibited a distinctly different B:O ratio of 0.17 and possible traces of silicon and sulfur.

**Table VII B:C and B:O Ratios of the Boron Powder Added SC1008 Char**

	No Sputtering	2 min Sputtering	4 min Sputtering
B:C	0.12	0.31	0.19
Deviation from Average (%)	-42	50	-8
B:O	0.37	1.60	1.06

X-ray photo electron spectroscopy (XPS) was used to characterize the 20% o-carborane added sample. Two different areas were investigated. From the XPS data it is clear that boron is existed in several different oxidation states. (Figures 21 & 22) Comparison of spectra collected from different areas shows that the main peak is at the same binding energy (191.5 eV). However, the line shapes of the spectra are different indicating inhomogeneity in the samples. The peaks do not correspond to any single oxidation state, they are probably a convolution of peaks intermediate between B<sub>4</sub>C and B<sub>2</sub>O<sub>3</sub>. (Table VIII) The B:C and B:O ratios of this sample was also determined to be 0.062 and 0.40 respectively. This shows good agreement with the results from SAM (see Table IX).

**Table VIII. Binding Energy for XPS**

Compound	Binding Energy ( eV)
B <sub>4</sub> C	186.3
B	190.3
B(OH) <sub>3</sub>	192.8
B <sub>2</sub> O <sub>3</sub>	193.1

Table IX shows the results of the Scanning Auger Microscopy (SAM) of these boron added SC1008 chars. The 8.6% B:C ratio of the 20% carborane char is in excellent agreement with the 8.52% boron content determined by EDS analysis. (see Task 2) Since there is about 30% unaccounted weight loss in the cure process, the good match between EDS and SAM results indicates that there is about 30 wt% carborane sublimed during the carbonization. Sublimation of carborane in phenolic resin is not uncommon as Baicher reported that about 15-20% of o-carborane was sublimed during the 1000°C pyrolysis of carborane added phenol formaldehyde type resins.<sup>7</sup>

**Table IX. SAM Results of the Boron Added SC1008 Char**

	o-Carborane			Powder Added		
	5%*	5%	20%			
B:C	0.043	0.056	0.086** (0.073, 0.082, 0.103)	0.12	0.31	0.19
B:O	0.39	0.16	0.44	0.37	1.60	1.06

\* Cleaved surface

\*\* Average value of three different measurements

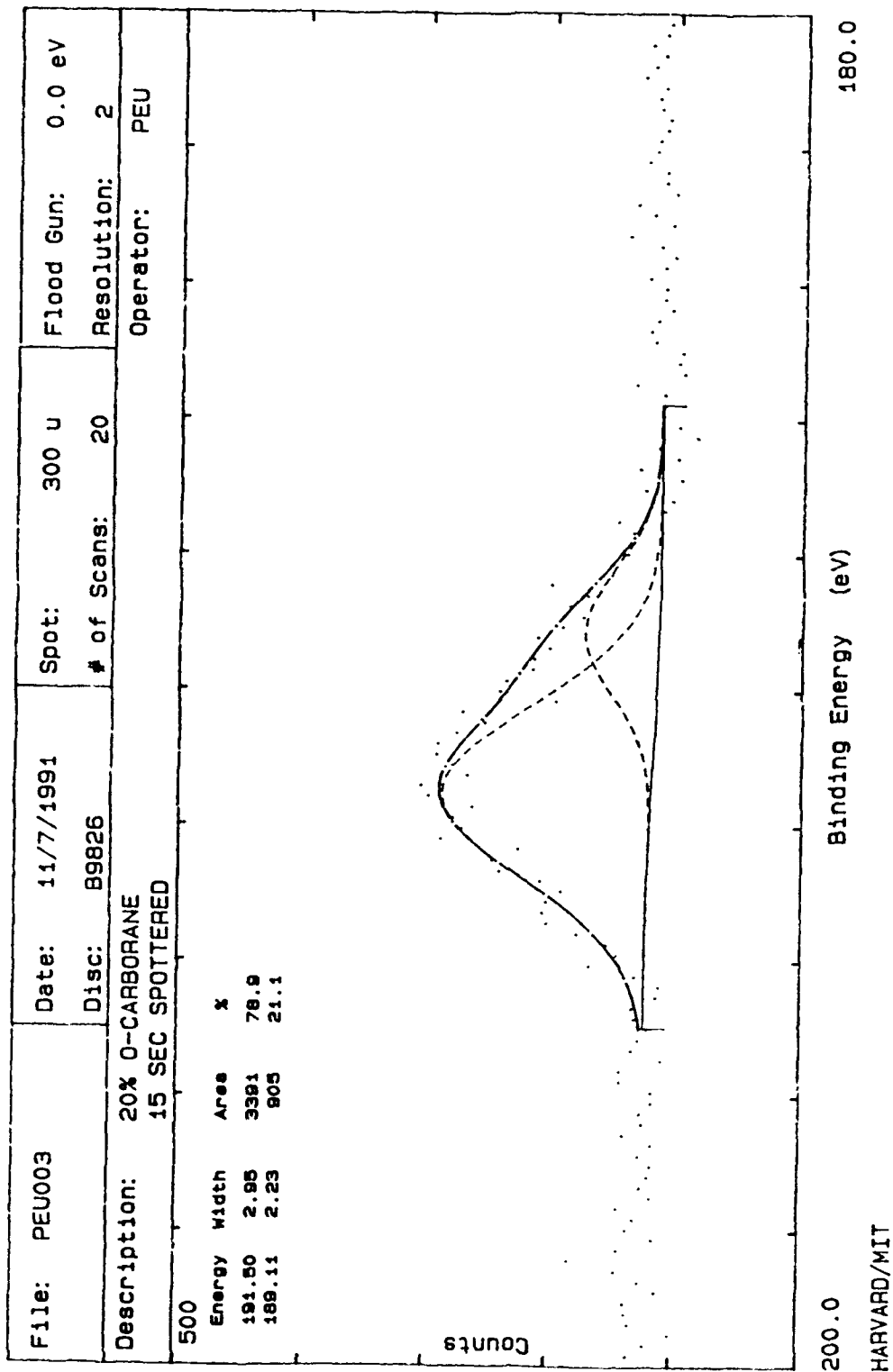


Figure 21. XPS Results of 20% o-Carborane Added SC1008 Char

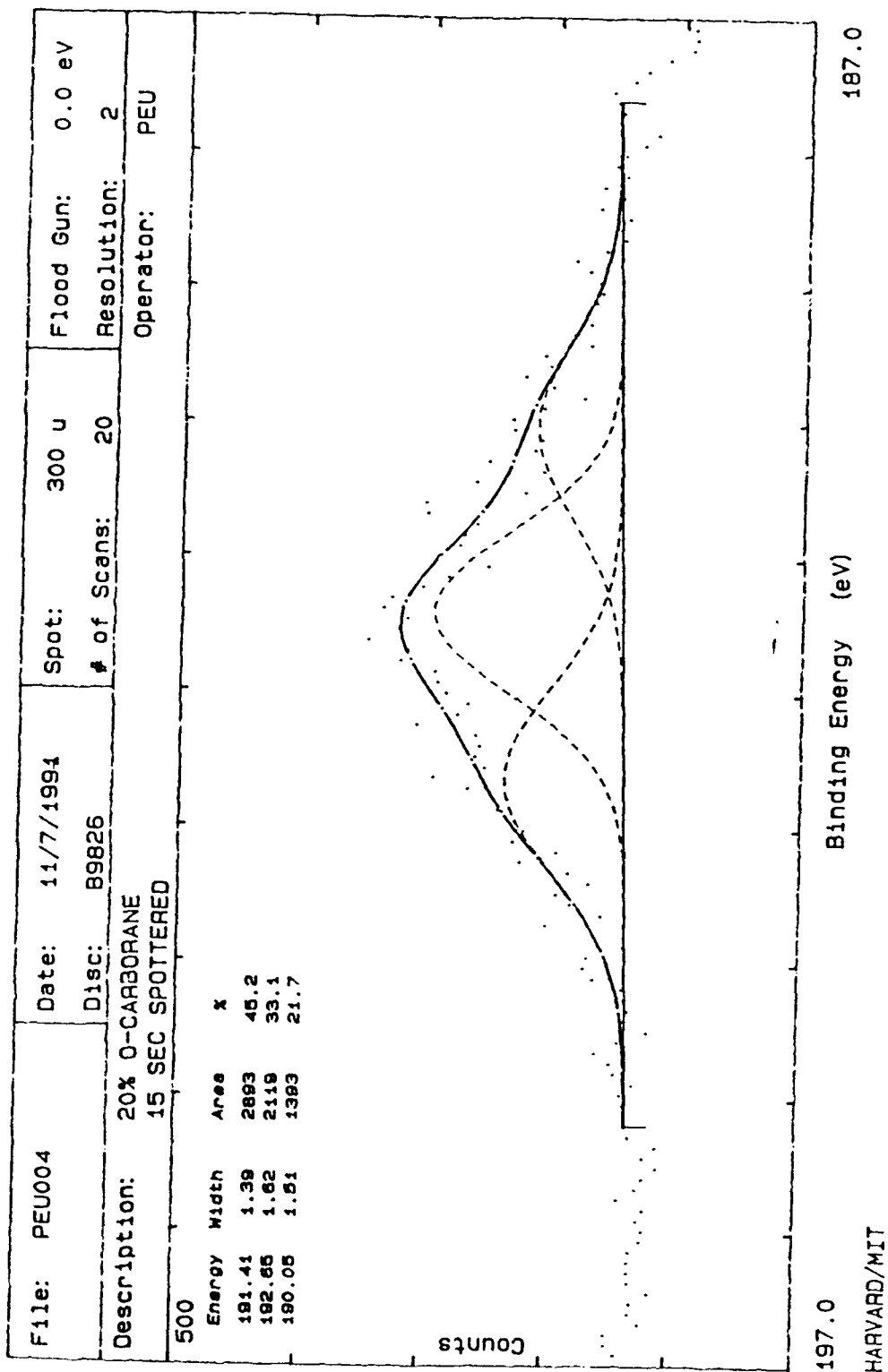


Figure 22. XPS Results of 20% o-Carborane Added SC1008 Char

This study indicates that the carborane added samples are more homogeneous than the powder added sample. The reliability of the B:C and B:O ratios for the 20% sample is also reflected by the good agreement between SAM and XPS analyses. A more thorough investigation, possibly including a complete mapping of the B:C ratio of a larger surface area, is required to get a better understanding of the magnitude of the inhomogeneity of boron in the carborane added samples.

#### Task 4. Characterization of Oxidation Resistance

Thermogravimetric analysis (TGA) was also used to characterize the oxidation resistance of the carbons. The as-cured phenolic resins were cut into small pieces and sent to Kaiser Aerotech, a well known manufacturer of carbon-carbon composites, for analysis. Each samples was carbonized in an inert atmosphere to 900°C at a heating rate of 10°C/min. After cooling down to room temperature, these samples were then oxidized in flowing air. The weight loss vs. temperature curves of the carbonization and oxidation process are shown in Figures 23-30. Carbonization of the SC1008 phenolic resin showed three main weight losses (rates of >1.0%/min.) at temperatures of 325, 460 and 600°C. For those samples with carborane additions, a wide band of weight loss at less than 500°C and a sharp weight loss at 670°C was observed. The boron powder sample behaved in a similar fashion to the SC1008 sample. The char yields of the SC1008, 5% carborane, 20% carborane and boron powder samples were 60.8, 70.6, 78.8 and 80.8 %, respectively, under this condition.

Oxidation of the SC1008 sample showed a reaction start at about 600°C and complete oxidation before 900°C. For the 5% carborane/SC1008 samples, an additional weight loss at 200°C of about 0.25%/min. was observed. At about 650°C, the carborane started to oxidize and a reduction in the rate of weight loss is noted. The boron powder sample behaved similar to the 5% carborane sample except that it picked up more weight after 700°C. The 20% carborane sample showed a sharp weight loss at 120°C. After this initial loss the sample did not lose any significant weight.

Oxidation testing of the modified phenolic resins by TGA indicated an early weight loss at temperature less than 500°C for all samples with boron additions, be it carborane or particulate. (Figure 31) Considering that these samples had been carbonized at 900°C and that the SC1008 phenolic did not show oxidation at temperature less than 600°C, this low temperature loss must be attributed to the added boron. Glasses high in B<sub>2</sub>O<sub>3</sub> degrade by hydrolysis under ambient conditions. Hydrolysis results in the formation of orthoboric acid (H<sub>3</sub>BO<sub>3</sub>) at low temperature.<sup>8</sup> Heating H<sub>3</sub>BO<sub>3</sub> above 100°C results in the release of water vapor and the formation of metaboric acid (HBO<sub>2</sub>). Above 250°C, HBO<sub>2</sub> begins to transform to B<sub>2</sub>O<sub>3</sub> with the release of water vapor. Theoretically about 2.5 wt.% of water will be released at temperatures greater than 100°C for each percent of boron.



TGA File Name: pc1  
 Sample Weight: 25.400 mg  
 Fri Sep 08 10:53:02 1991  
 cured phenolic resin.

PERKIN-ELMER  
 7 Series Thermal Analysis System  
 N<sub>2</sub>

TGA 1st Derivative: pc1  
 Sample Weight: 25.400 mg  
 Fri Sep 08 10:53:02 1991  
 cured phenolic resin.

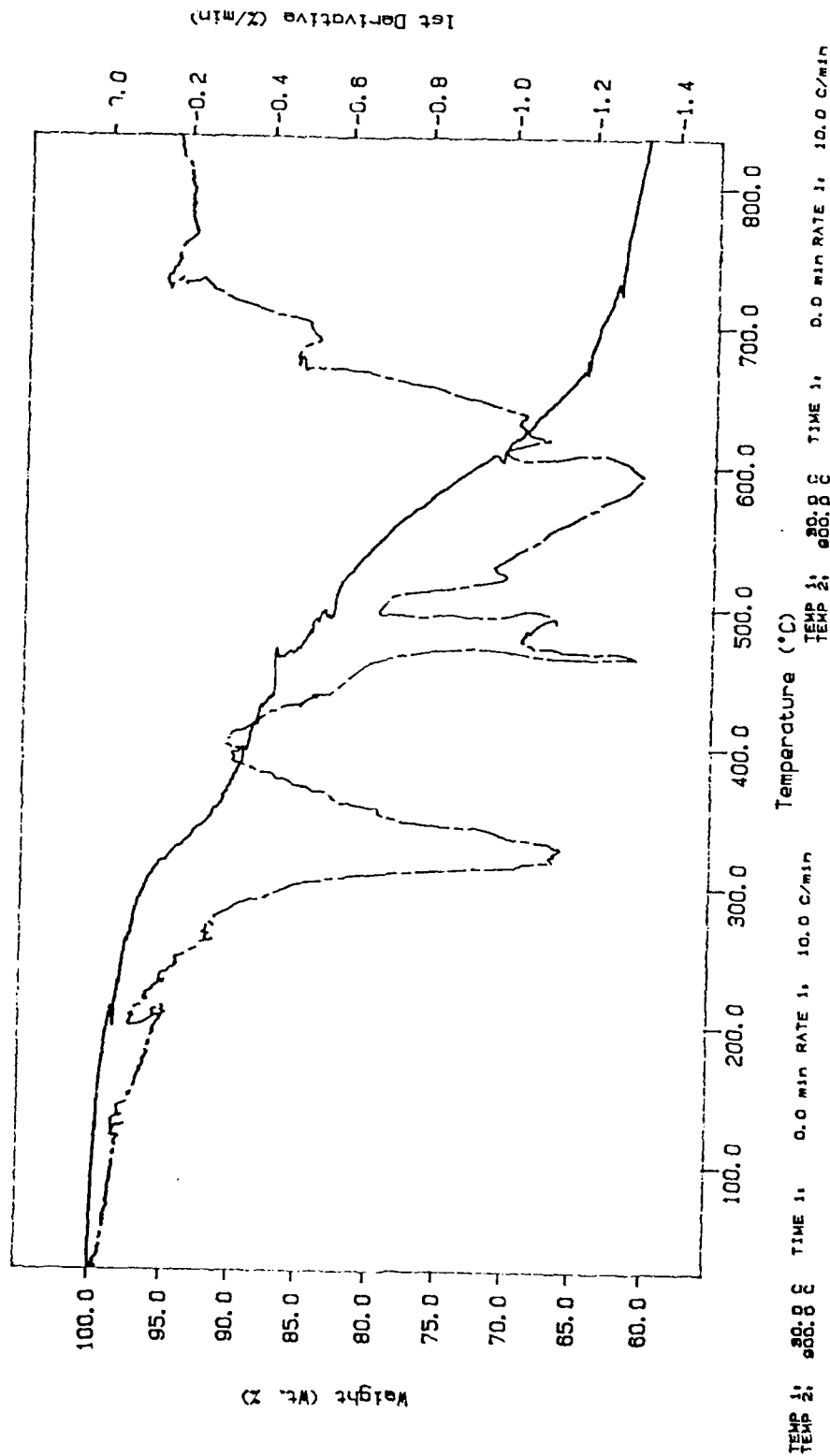


Figure 23. TGA Results, Carbonization of SC1008

TGA File Name: pc1a  
 Sample Weight: 15.853 mg  
 Wed Sep 11 16:05:45 1991  
 Cured SC1008 -

PERKIN-ELMER  
 7 Series Thermal Analysis System  
 in air

TGA 1st Derivative: pc1a  
 Sample Weight: 15.853 mg  
 Wed Sep 11 16:05:45 1991  
 Cured SC1008 - in air

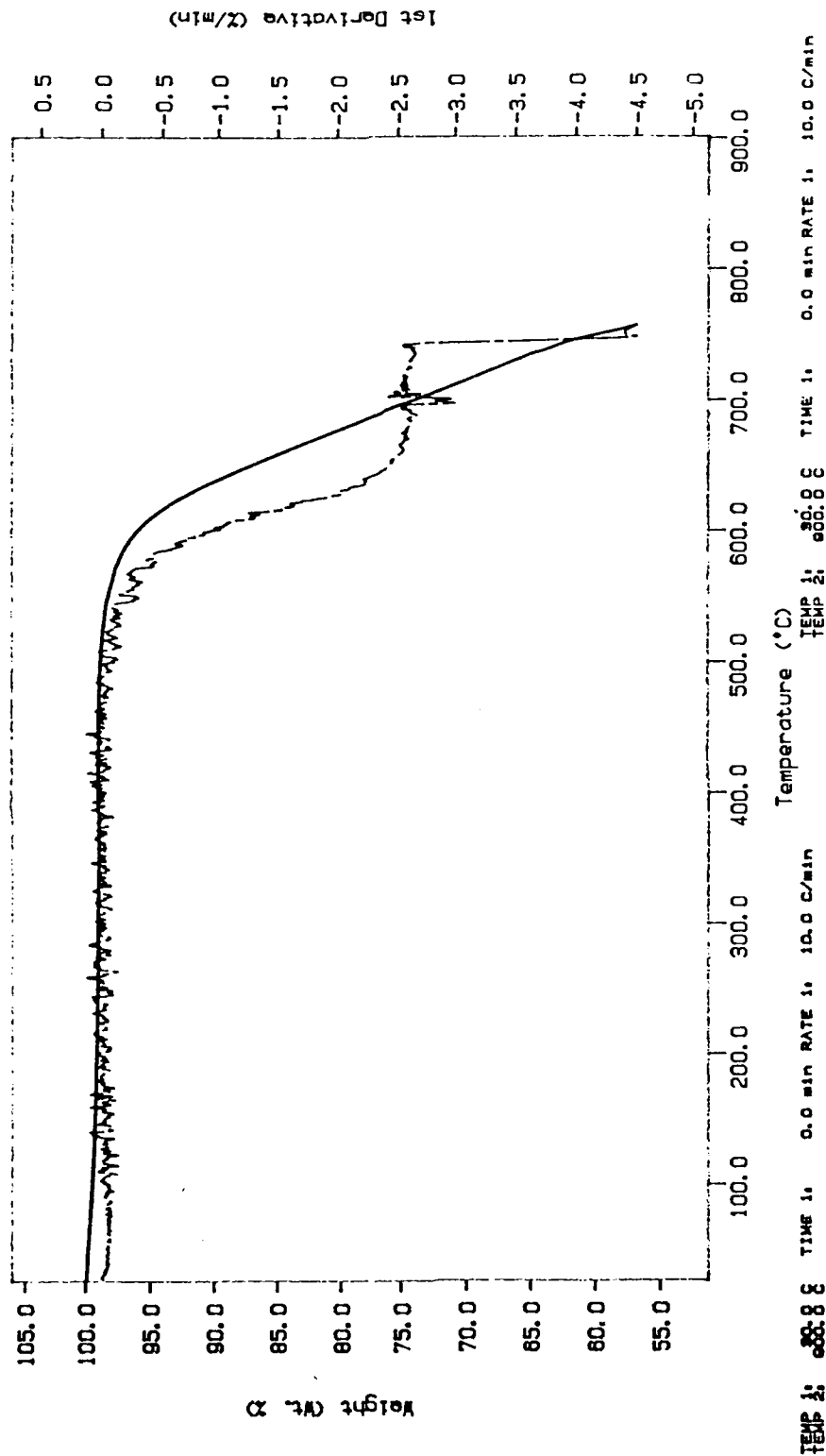


Figure 24. TGA Results, Oxidation of SC1008

TGA File Name: phil2  
 Sample Weight: 29.646 mg  
 Fri Sep 06 15:36:36 1991  
 5% o-carborane -  
 in nitrogen  
 PERKIN-ELMER  
 7 Series Thermal Analysis System

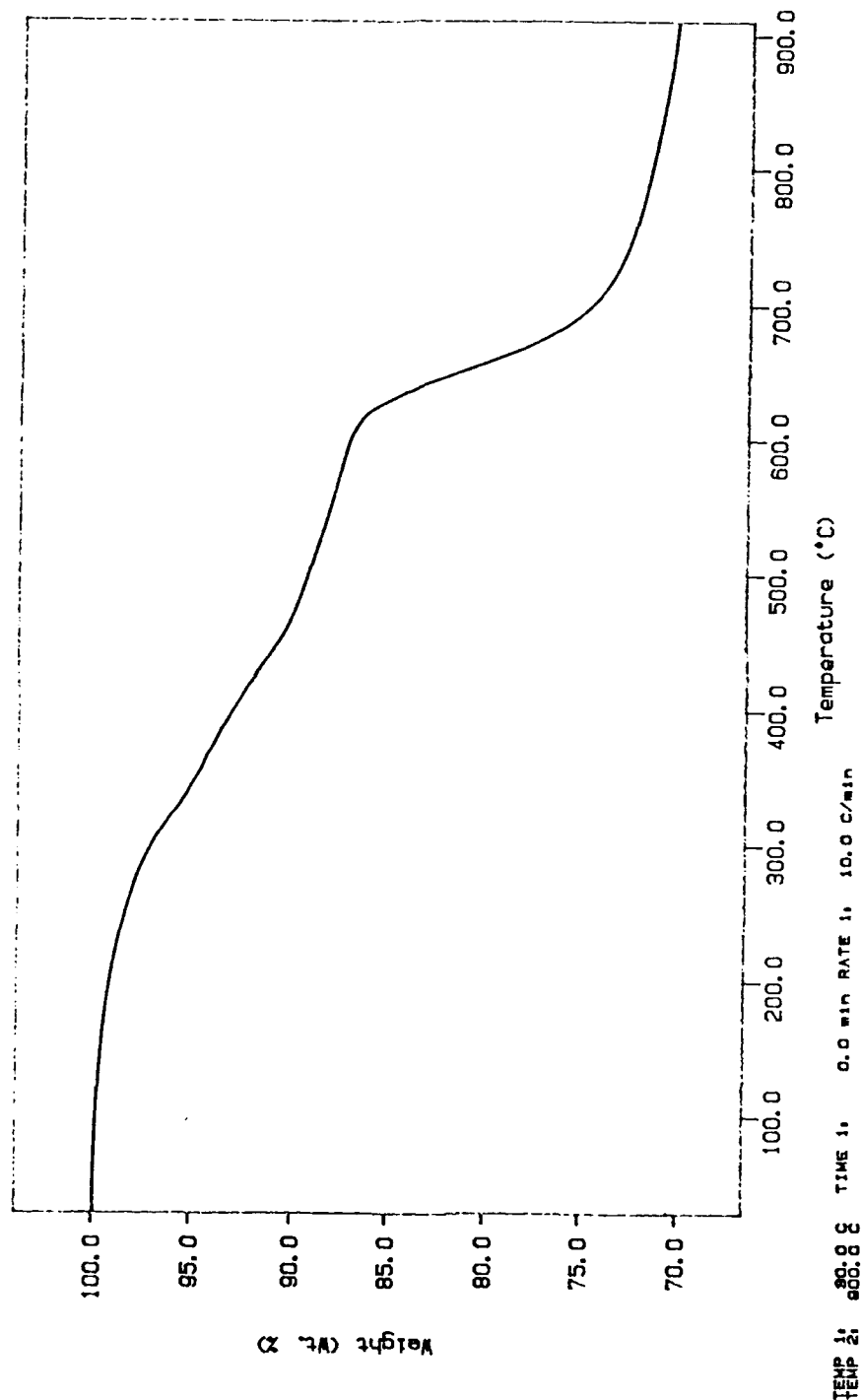


Figure 25. TGA Results, Carbonization of 5% Carborane Added SC1008

TGA File Name: pc2a  
 Sample Weight: 22.832 mg  
 Thu Sep 12 11:38:48 1991  
 5% O-Carborane, after carb. in air

PERKIN-ELMER  
 7 Series Thermal Analysis System  
 5% O-Carborane, after carb. in air

TGA 1st Derivative: pc2a  
 Sample Weight: 22.832 mg  
 Thu Sep 12 11:38:46 1991  
 5% O-Carborane, after carb. in air

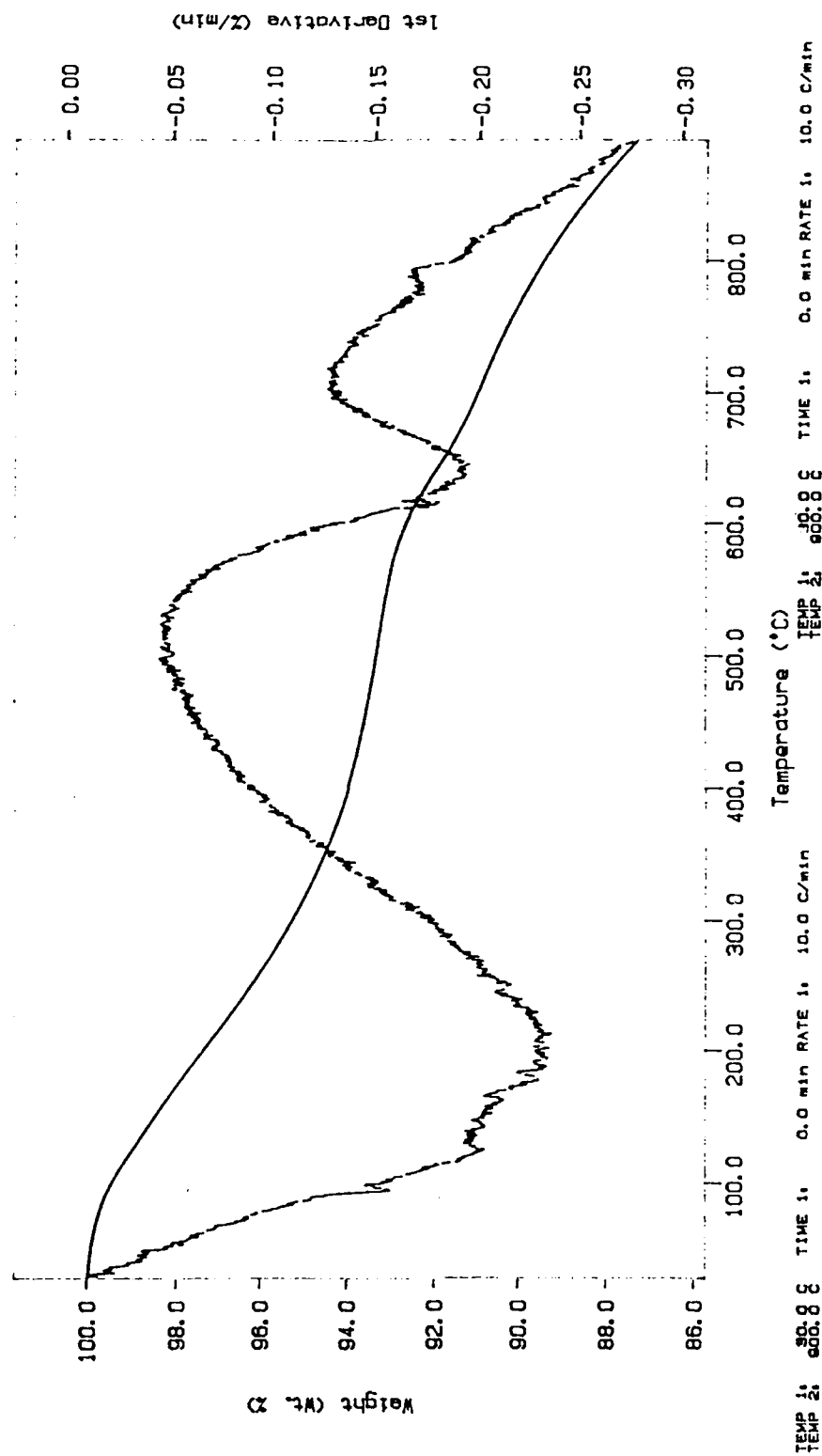


Figure 26. TGA Results, Oxidation of 5% Carborane Added SC1008 Char

TGA File Name: phil3  
 Sample Weight: 10.012 mg  
 Sat Sep 07 11:26:36 1991  
 20% 0-carborane.

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: phil3  
 Sample Weight: 10.012 mg  
 Sat Sep 07 11:26:36 1991  
 20% 0-carborane.

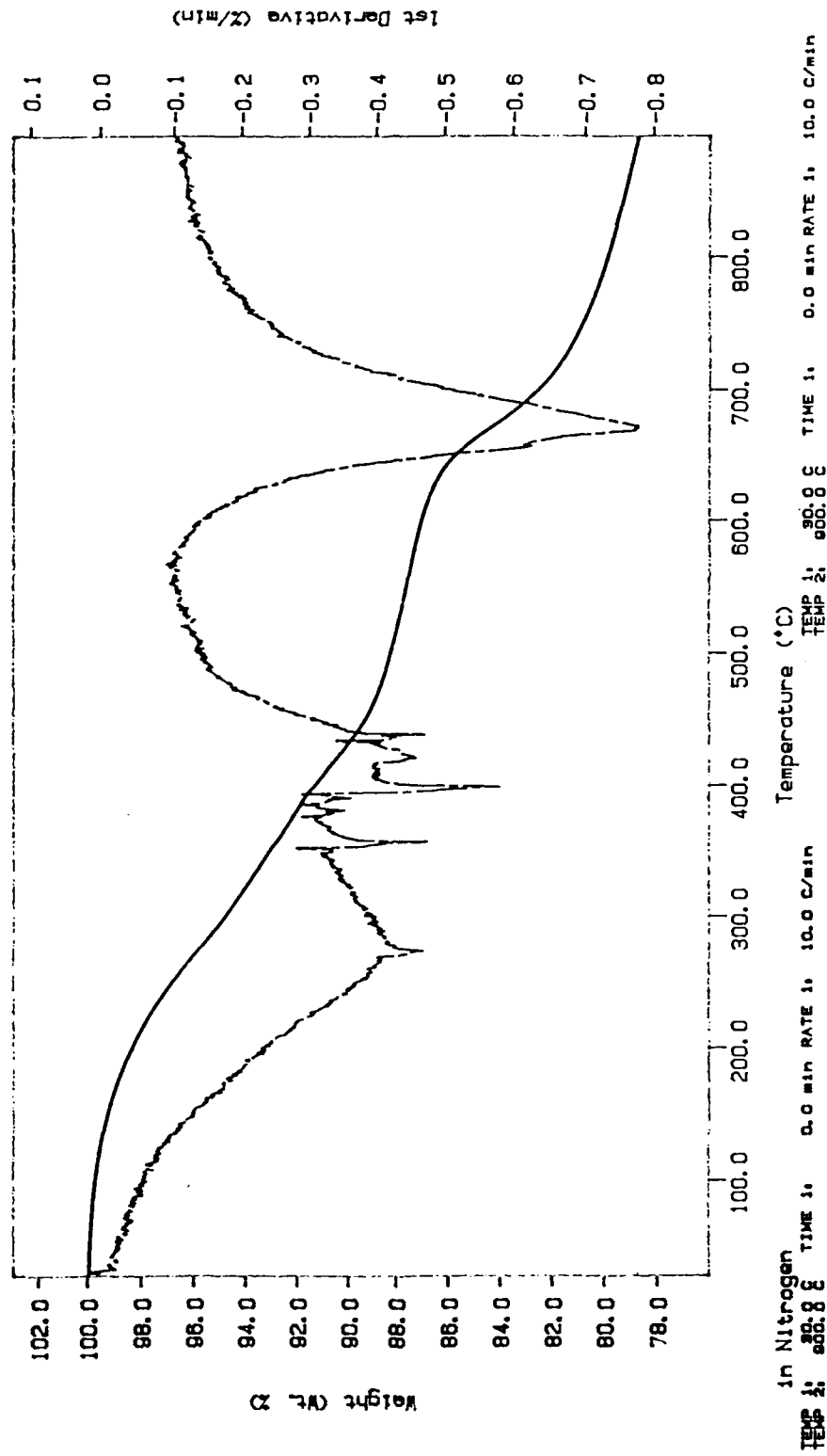


Figure 27 TGA Results, Carbonization of 20% Carborane Added SC1008

TGA File Name: pc3a  
 Sample Weight: 8.558 mg  
 Thu Sep 12 14:08:50 1991  
 20% O-Carborane, after carb. in air

PERKIN-ELMER  
 7 Series Thermal Analysis System  
 20% O-Carborane, after carb. in air

TGA 1st Derivative: pc3a  
 Sample Weight: 8.559 mg  
 Thu Sep 12 14:09:50 1991

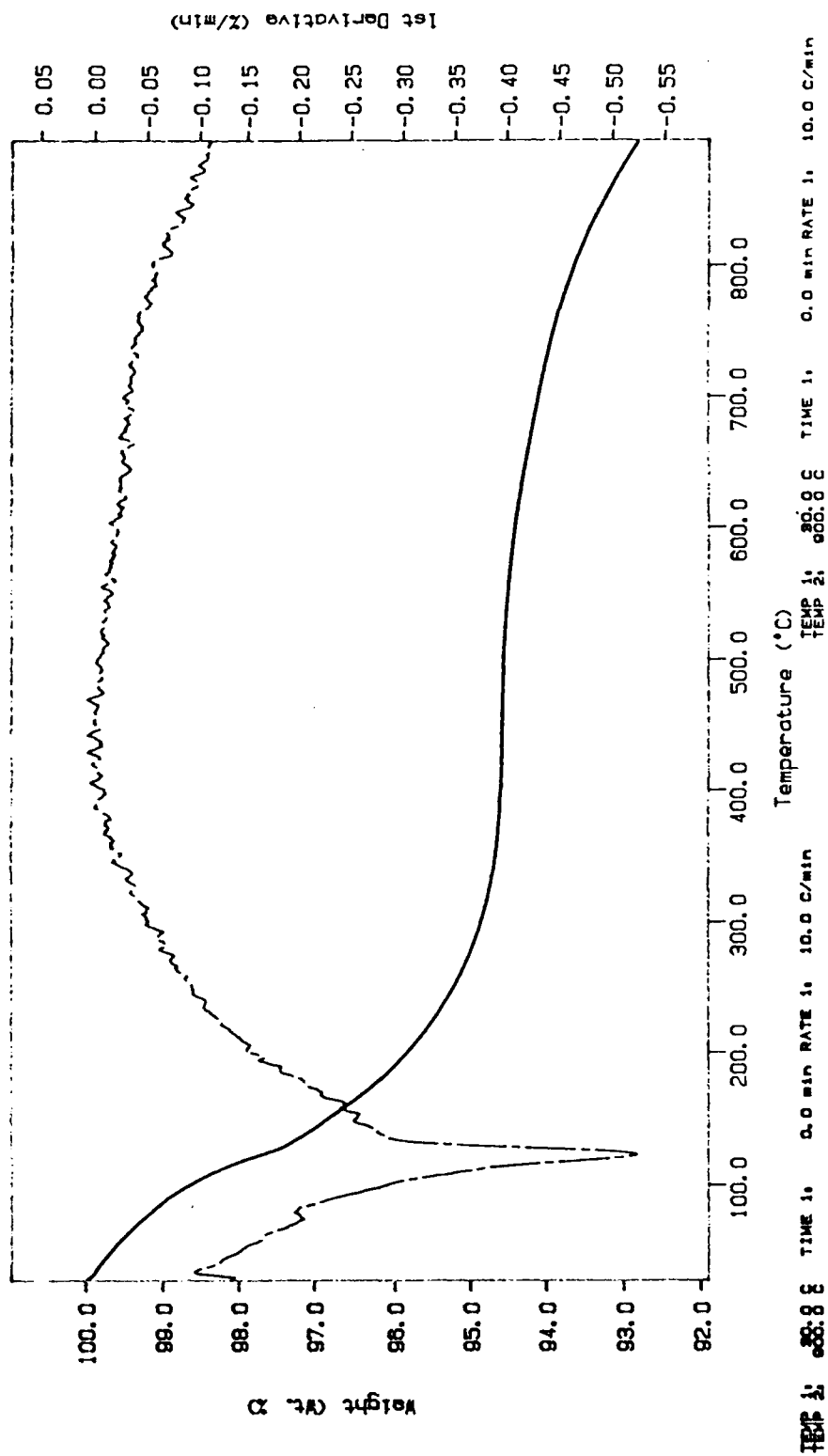


Figure 28. TGA Results, Oxidation of 20% Carborane Added SC1008 Char

TGA File Name: phil14  
 Sample Weight: 34.417 mg  
 Sat Sep 07 13:46:08 1991  
 powder added

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: phil14  
 Sample Weight: 34.417 mg  
 Sat Sep 07 13:46:08 1991

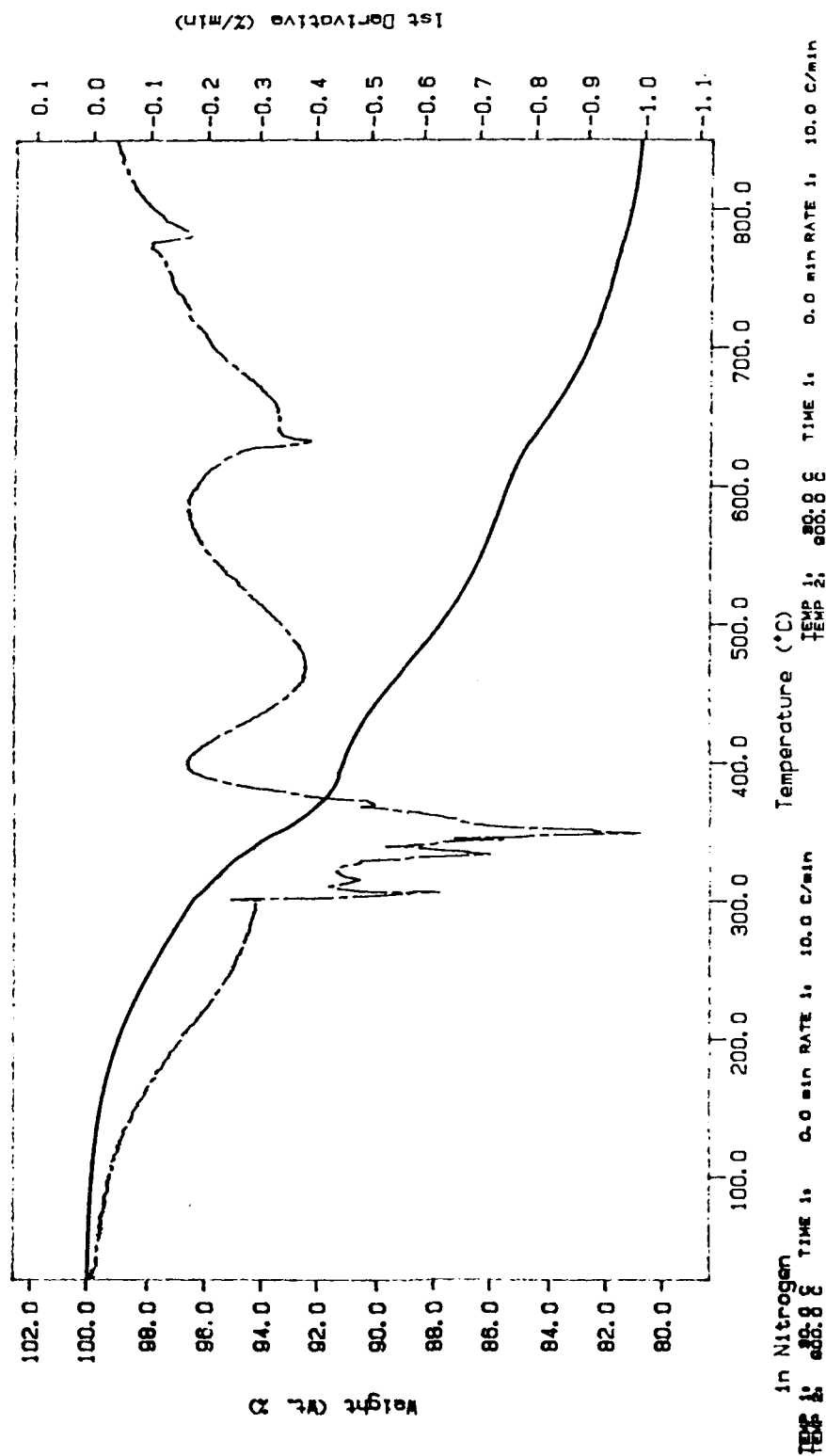


Figure 29. TGA Results, Carbonization of Boron Powder Added SC1008

TGA File Name: pc4a  
 Sample Weight: 28.530 mg  
 Thu Sep 12 16:26:48 1991  
 powder added after carb. in air

PERKIN-ELMER  
 7 Series Thermal Analysis System

TGA 1st Derivative: pc4a  
 Sample Weight: 28.530 mg  
 Thu Sep 12 16:26:48 1991  
 after carb. in air

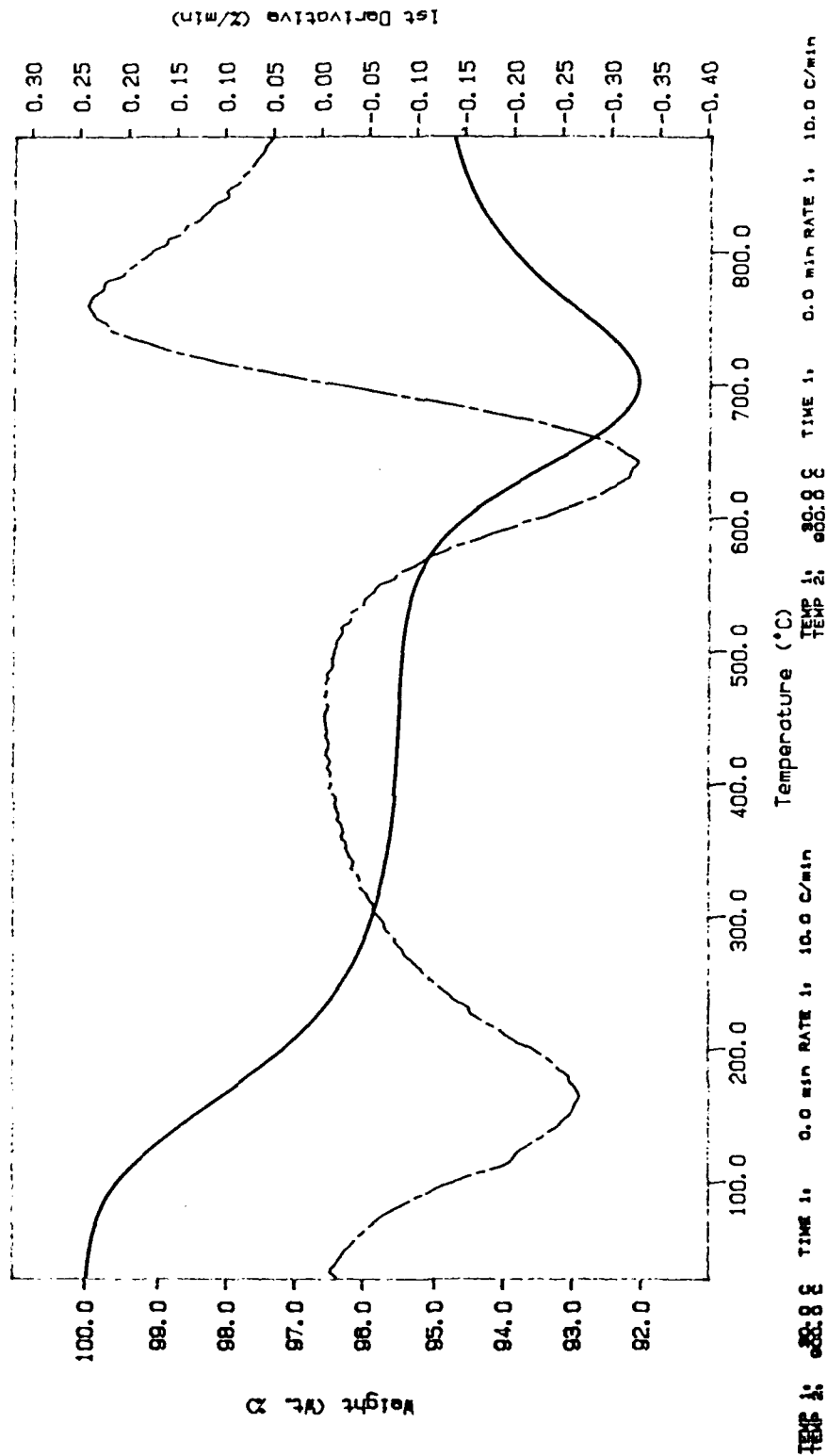
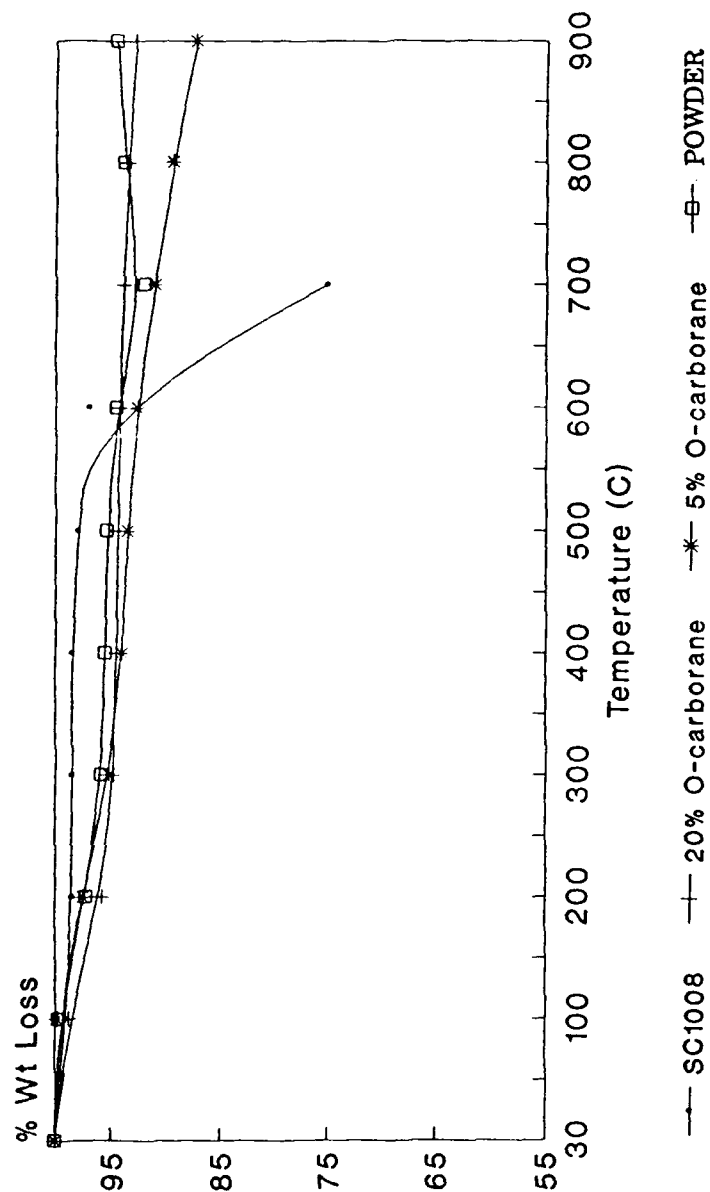


Figure 30. TGA Results, Oxidation of Boron Powder Added SC1008 Char



# TGA testing in air % Wt loss vs. Temp (C)



Heating rate = 10 C/min

Figure 31. TGA Results, Boron Added SC1008 Chars

From the sample weights prior to the TGA oxidation tests, the 5% carborane, 20% carborane and powder added sample picked up 6.56, 6.75 and 5.0 wt.% moisture respectively in 5 days when stored in a dessicator. Most of these weight gains were released at temperatures well below 600°C. As the temperature reached 600°C, samples lost weight as a result of carbon oxidation. With increasing temperature, the boron reacts with enough oxygen to make up the weight loss. The TGA oxidation curve of the powder added sample showed this weight gain from oxygen pick-up at temperature greater than 700°C.(Figure 26)

#### Task 5. Estimation of the Cost for Large Scale Production

Carborane is an expensive chemical. It is commercially available (Dexsil Co. Hamden, CT) and costs \$19/gram (\$8,626/pound). Since the conversion of decaborane to o-carborane has a yield of about 90%, the high cost of decaborane (\$10/Gram), is responsible for this high price. For a single large scale production run (100-1,000 pounds), the cost of decaborane is reported to be about \$1,200 - \$1,500/lb (Callery Chemical, Pittsburgh, PA). Given the high conversion yield, the cost of carborane is expected to be less than \$2,000/pound. Constancy of large demand is expected to result in further reductions in price.

In spite of the high cost of this boron source, its use in the carbon-carbon composites might be justified. Commercial unprotected carbon-carbon composite panels (K-Carb from Kaiser Aerotech, San Leandro, CA) cost about \$200/pound. These composites are reinforced with low strength rayon based carbon fiber. For aerospace applications, high strength T-300 reinforcement is required. The price for these composites range from \$250/pound for flat panels to \$350/pound for complicated structures. These carbon-carbon composites consist of about 30 wt% of matrix. It takes about 0.6 lb of phenolic resin to yield one pound of composite assuming about 50% total yield (70% cure yield and 75% char yield). Since the actual production process involves material loss, it may take over one pound of phenolic resin for composite fabrication. With a 5% carborane addition, and assuming recovery of 80% of the sublimed carborane, there is an extra cost of about \$53 (0.06 lb carborane at \$1,200/lb). This is only about 13-20% of the composite cost. Current powder based systems comprise ~10% of the cost of the composite.

#### **Conclusions**

Atomic dispersion of boron in phenolic resin, through the additions of carboranes, increased the yield and improved the oxidation resistance of the char. Small amount of boron addition, as little as 3%, dramatically improved the oxidation resistance of the phenolic char. An 11.3% boron was estimated to be required for complete oxidation protection. To achieve this boron content, the chemical structure of carborane was modified by attachment of carboxylic acid.

Distribution of boron in the chars, as studied by SAM and XPS indicated that the samples with carborane additions are more homogeneous than the samples with powder additions. This homogeneity of boron distribution contributed to the

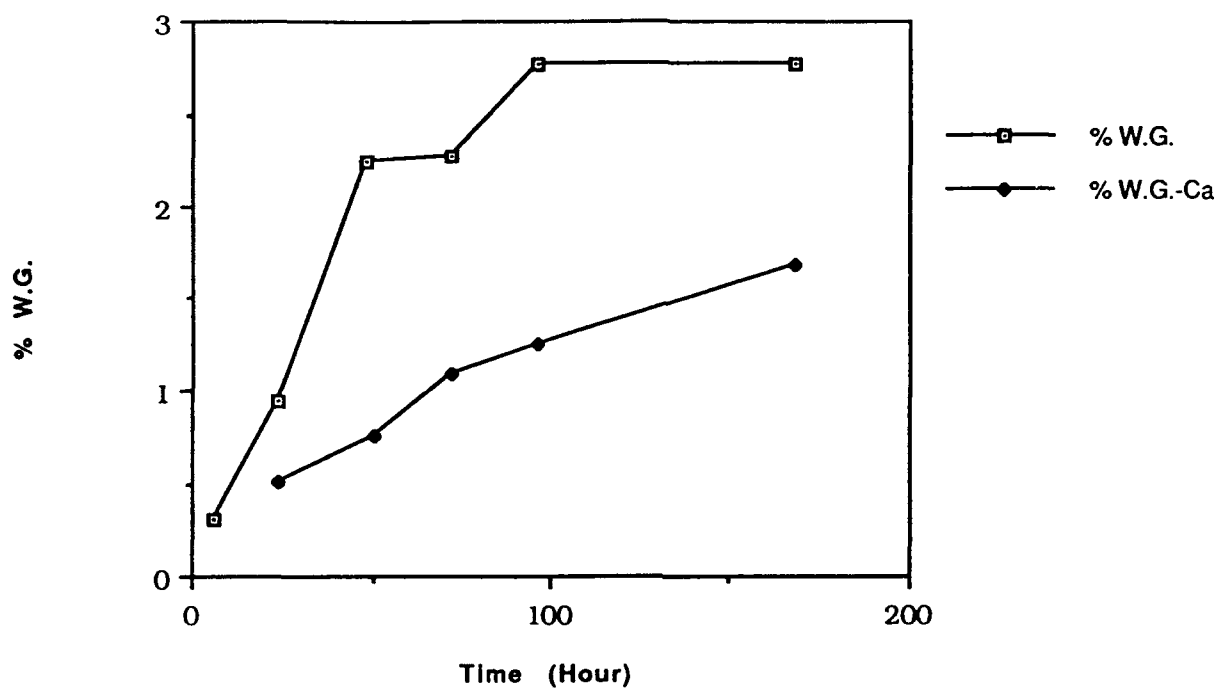
achievement of oxidation resistance with less boron content. Good agreements existed between the boron characterization from EDS, SAM and XPS techniques.

## Recommendations

TGA oxidation tests of the phenolic chars highlighted the moisture sensitivity of the boron modified systems. Moisture attack problems with boron addition must be addressed as the absorbed water will convert to steam under rapid heating. Steam release aggravates localized stress problems and provides additional oxidizing species. Alkali additions have been known to improve the moisture resistance of  $B_2O_3$ .<sup>9</sup> Addition of 20 mole% of  $Li_2O$  reduced the leaching rate of  $B_2O_3$  two orders of magnitude.<sup>10</sup> Unfortunately, lithium oxide compounds, the least volatile and most stable alkali oxides, are not stable within boron-modified carbon-carbon composites at even minimal processing temperatures. However, alkaline earth additions can also benefit the moisture resistance of  $B_2O_3$ . A 20 mole%  $CaO$  addition was found to be very resistant to hydration and leaching.<sup>6</sup> Incorporation of alkaline molecules, such as Ca and Ba, are expected to improve the moisture resistance of the boron modified systems.

Several organometallic calcium sources are now commercial available as a result of superconductor research. One of these precursors, Ca-2-ethyl hexanoate, is in liquid form and miscible with SC1008 phenolic resin. About 49 wt% of Ca-2-ethyl hexanoate (Strem Chemical, 40% pure, 3-4% Ca) was mixed with 5% carborane added SC1008 and cured in air following the cycle previous described. Moisture pick-up of the carbonized sample was monitored and compared with the 4.7% CAPCME added sample. Figure 32 shows the results. Addition of calcium element into the boron modified phenolic reduced the moisture attack significantly. Additions of calcium rich compounds would reduce the amount of additive required.

Although the carborane improved oxidation resistance and yield, the relative high cost of the chemical could limit it from commercial applications; consequently, less expensive boron sources need to be explored. Alkyl borates, a stable and inexpensive compound, may be the alternative for boron sources. Although the formation of  $B_2O_3$  during the process is reported to be detrimental to the oxidation resistance of boron powder added carbon-carbon, cursory experiments suggest this is not the case for atomically dispersed boron systems. Addition of 33% tributylborate (TBB), an inexpensive boron source, into SC1008 did show improvement in the oxidation resistance of the phenolic char (33% weight loss after one hour at 900°C) even though TBB has a boron content of only 5.9%. Higher boron content borates, such as trimethylborate, should also be examined.



**Figure 32. Weight Gain of Calcium Added Sample**

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